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The textbook outlines the basics of ground water theory and provides brief and comprehensive information on such important issues of hydrogeology as water resources and their availability, ground water origins and distribution over the Earth, main hydrogeological units and systems, hydraulic properties of soils and rocks, basic equations of ground water flow. The special chapter is devoted to environmental hydrogeology, particularly, ground water chemistry, major contaminants and chemical transformations in ground water.

This textbook is intended for students in geology and mining.

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CONTENTS

Preface.....	4
1. Water resources and their distribution over the Earth's surface.....	6
1.1. Total reserves and availability.....	6
1.2. The latest trends in the world's water resources use.....	9
2. Groundwater formation.....	16
2.1. Water in the Earth's crust.....	16
2.2. Geological characterization of ground water origin.....	20
2.3. Hydrological cycle.....	23
3. Aquifers.....	31
3.1. Ground water system.....	31
3.2. Aquifer types.....	35
4. Hydraulic properties of soils and rocks.....	40
4.1. Storage properties.....	40
4.2. Hydraulic head.....	47
4.3. Heterogeneity and anisotropy.....	53
5. Ground water flow.....	57
5.1. Flow equations.....	57
5.2. Initial and boundary conditions	61
6. Ground water chemistry	66
6.1. Species in groundwater.....	66
6.2. Ground water contaminants.....	71
6.3. Basic chemical reactions in ground water.....	84
Glossary.....	90
Nomenclature.....	97
Bibliography.....	98

PREFACE

According to F. Savarenskiy the subject studied by hydrogeology is ground water, its origin, occurrence conditions, movement, properties and conditions of applying certain technical measures to ground water use, regulation and disposal [58]. Hydrogeology is the part of geology and based on the analysis of Earth's crust development. In other words, hydrogeology studies the geology of water.

Ground water has been used for drinking and household purposes for a long time. Nowadays, it is the major source of urban drinking water supply in most European countries with the dominant share of ground water in the overall drinking water supply. In such countries as Saudi Arabia, Kuwait, Denmark, and Malta, groundwater is the only source of natural water.

Ground water is widely used for medicinal purposes. Many important chemical elements are extracted from ground water; among them are boron, sodium, magnesium, lithium, chlorine, bromine, iodine etc. Over the last decades, ground water has been increasingly used as a source of thermal energy.

However, in some cases ground water plays a negative role, particularly, during construction and operation of hydropower facilities, tunnels, and subways. Ground water inflows are unavoidable in underground and open pit mining, which causes many environmental after-effects and requires proper mine drainage.

Apart from hydrogeology, natural waters are also studied in some aspects by various sciences including oceanography, hydrology, meteorology, glaciology, hydraulics. Within the framework of hydrogeology a number of scientific areas are developing, some of them are briefly defined below [60].

General hydrogeology studies the structure, composition, and most common properties of the subsurface hydrosphere, the patterns of water distribution, and its occurrence below the ground surface, the role of water in the Earth's geological development [17].

Subsurface hydrology studies various forms of groundwater flow taking into account the specific structure of subsurface flow, depending on local geological features.

Ground water chemistry studies the features of subsurface migration of chemical elements and compounds within the three-phase system “water – rock – gas” containing also organic matter. Ground water chemistry focuses on identification of various geochemical types of groundwater, as well as prediction of ground water quality.

Regional hydrogeology describes how the development and features of geological structures have influenced the spatial and temporal distribution of ground water and its composition in Earth's crust and a particular region.

Environmental hydrogeology studies the direct and indirect impacts on ground water resulted by construction reservoirs on rivers and retention ponds for mine water storage, deforestation, mining, and other human activities. Environmental hydrogeology addresses the issue of effective use and management of ground water resources in terms of environment and climate changes.

Applied hydrogeology includes some specific areas linked with mining of solid minerals (coal, ores), oil and gas extraction, ground water search and exploration, drilling and operation of boreholes, ground water protection, rehabilitation and land reclamation after mining and other industrial activities, prospecting of mineral deposits, urban planning etc.

Mapping is one of the widely applied techniques in hydrogeology, which is used primarily for quantitative analysis of regional aquifer patterns. The subsurface hydrosphere is the product of geological and anthropogenic development. Therefore, studying ground water systems requires reproducing all stages of their development and prediction of possible changes.

Regarding the complexity of water movements in soils and rocks such prediction can be performed using various methods of mathematical modeling, laboratory studies, and field experiments. *Modeling* as the tool for numerical analysis of ground water systems is getting increasing importance in modern hydrogeology.

This book addresses the key issues of hydrogeology. Particularly, Chapter 1 describes ground water resources and their availability around the globe. Chapter 2 characterizes ground water formation, water balance and hydrological cycle. Chapter 3 defines hydrogeological units as the elements of aquifer systems, quantifies rock and soil properties crucial for characterization of ground water flow. Chapter 4 presents the basics of ground water flow in saturated and unsaturated soils. Chapter 5 describes ground water properties and its chemical composition.

The author will appreciate any comments and remarks aimed to improve the contents and structure of the textbook.

1. WATER RESOURCES AND THEIR DISTRIBUTION OVER THE EARTH'S SURFACE

1.1. Total reserves and availability

World's water resources. Factors affecting fresh water availability.

World's water resources. The total land area covered with liquid water on the Earth is about 380 million km² or 75% of the total globe surface (Table 1.1). This figure refers to only the lower limit of the water surface because it actually varies depending on the season. Every year snow alternatively covers huge areas of land in the northern and southern hemispheres, with the especially large area occupying more than 42 million km² in the northern hemisphere [10].

Water in liquid, solid, and gaseous state forms the hydrosphere.

Table 1.1

Distribution of water over the Earth's surface

	Ocean	Glaciers	Lakes and rivers	Swamps and wetlands	Snow cover	Total
Area, million km ²	361,2	16,3	2,3	≈3,0	≈42,0	≈443
% of Earth's surface	70,8	3,2	0,45	0,6	8,2	86,9

The volume of ocean water is about 1320 million km³, the estimated water volume of polar ice caps and glaciers on the continents is about 30,4 million km³. Freshwater lakes contain 125 thousand km³ of water, and saline lakes and inland seas contain 104 thousand km³.

The biggest fresh water reserves are concentrated in Lake Baikal in Russia, which equals 23 thousand km³ or 20% of fresh water stored in natural water bodies of the globe. This volume is approximately the same as that contained in Great Lakes in North America (Superior, Michigan, Huron, Erie, and Ontario). The Caspian Sea, the Dead Sea, and the Great Salt Lake are among the major salt lakes in the world. Artificial water bodies including ponds, reservoirs on rivers, and channels contain 4286 km³ of water.

The depth of most wetlands range from 0 to 2 m; their total volume of water is estimated from 2300 to 2900 km³. The main root zone contains 25000 km³, and the accessible fresh water stored in rocks is estimated at 4,17 million km² of water.

Generally, the global water supply is about 1358 million m³, with 97% accumulated in the oceans. The total volume of fresh and saline water in the land and subsurface is estimated at 39 million km². About 78% of this water is stored in icecaps and glaciers; most of this is inaccessible for the use because is concentrated in Greenland and Antarctica, far from human activities. Much of the ground water at

the depths of more than 800 m is also economically inaccessible or saline. Therefore, less than 3% of the world's fresh water supply is available on the continents, and only 11% of this water is actually usable and accessible. The water reserve distribution is shown in Fig. 1.1.

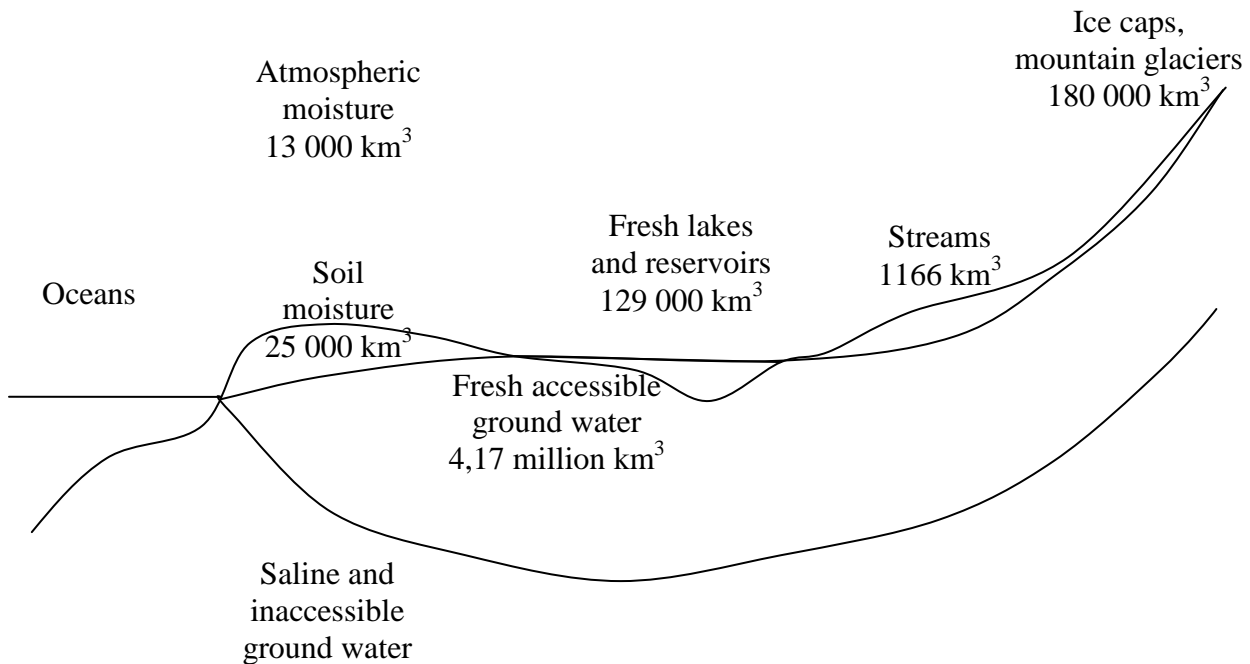


Fig. 1.1. Volumes of global water supply constituents [37]

Although the above mentioned estimates are approximate, they are useful to understand the importance of water management and water supply for various human, industrial, and agricultural activities. In the last decades the desalinization process is becoming more feasible. In 2010, about 16 000 desalinization plants in the world produced roughly 70 million m³ of potable water daily [71]; more than half of this amount was treated using the reverse osmosis technology. The number of desalinization plants is growing rapidly, especially in Gulf countries, North Africa, USA, Southern Europe, South East Asia; the cost of this water is getting more affordable and continues to decline.

Nevertheless, the most of water supply in the world is currently provided by available ground and surface waters. Moreover, for inland areas natural waters will remain the major resource sustaining various human activities. The inland areas are receiving water from seas indirectly, as vapor is carried in the air and dropped as precipitations.

Factors affecting fresh water availability. The acute problem of the water industry today is the possible impacts of climate change on water resources availability, which is especially important and crucial for the planning of water management. The better-known and most threatening trends are reduction of snow cover, melting of mountainous glaciers, shrinking of large inland seas and lakes.

The fourth large lake in the world, the Aral Sea located in the center of Euro-Asian continent has shrunk dramatically over the past decades. Two main rivers,

Amu-Darya and Syr-Darya feed the basin of about 1,8 million km². The diversion of millions m³ of water from these rivers for irrigation of cotton fields and rice paddies has contributed to the increase in agriculture production on 8 million hectares. The human interventions have radically changed the water system of this basin. In 1965 the Aral Sea received 50 km³ annually; in the early 1980s this amount fell to zero. As a result, salinity of water in the shrinking body of the sea reached 33 g/L, which is three times more than the initial value of 10-12 g/L. The shrinking of the Aral Sea has also affected the regional climate; air temperature in the shore zone has increased by 1,5–2,5 °C [22]. The mean annual relative air humidity decreased by 23%. The secondary effects of the Aral Sea reduction are the exposure of the lakebed, and soil and air contamination as a result of strong wind blowing off the soil grains.

Lake Chad is Africa's fourth largest lake by surface area; its basin covers the area of 2,5 million km². This lake was the water source for many agricultural projects. Besides, the region suffers from an increasingly dry climate, aggravated by the decrease in rainfall since 1960s. The today's size of the Lake Chad is only 1/20th of the size it was 35 years ago [47]. Despite high evaporation rate (2000 mm/year), water in the rest of the lake has surprisingly low salinity, from 120 to 320 mg/L. This concentration is remaining relatively stable owing to such factors as significant dilution of rainfalls, low salinity of the input rivers, seepage through the lake bottom to the ground water level, and biogeochemical regulations.

Lake Superior in North America, the world's largest fresh water lake has been shrinking and is getting hotter; some researchers believe these processes are interrelated [42].

To quantify the water availability the Food and Agriculture Organization of the United Nations (FAO) has derived the index of Total Actual Renewable Water Resources (TARWR) [14]. It is a calculated volume per year (km³/year) divided by the country population and expressed as a per capita volume available for the inhabitants. This index takes into account a number of many specific indicators including

- internally generated surface water runoff and ground water recharge derived from precipitations within the country's borders;
- external flows from neighboring countries contributing to both the surface and ground waters;
- subtracting any potential resources shared by the same water, this comes from surface and ground water interactions;
- subtracting any flow volume required by a treaty to leave the country borders.

TARWR is the maximum theoretical amount of water available for the country and renewable annually as surface water runoff and ground water recharge. When using TARWR the following factors should also be taken into account:

- approximately 27% of the world's surface runoff occurs as floods that are considered as actually unusable;
- seasonal variability in precipitation is not correctly described in average annual figures;

- differences in climatic zones and population density are not taken into account.

Not all of the internally converted fresh water resources can be controlled by the population. Only about one third of these resources can be potentially controlled, in case of using most feasible technical, social, environmental, and economic means. The global potentially usable water resources are estimated within the range from 9000 km³ to 14000 km³. At present, about 2370 km³ of the global potentially usable water resources are diverted as the primary water supply or the first water supply for human use. The other part returns to rivers, streams, and aquifers, and actually, this recycled part is again withdrawn for human use. The primary water supply and recycled water supply (about 3300 km³) constitute the water used in agriculture, industry, and municipal supply.

1.2. The latest trends in the world's water resources use

Water use. Ground water use in Europe and Ukraine, Africa, the USA, China and India, the Middle East and North Africa. Water scarcity. Climate change impacts on ground water.

Water use is a general term referring to water used for specific purposes including domestic water supply, irrigation, and industrial processing. Water use influences the hydrological cycle and includes [37]

- water withdrawals from ground and surface waters;
- water transportation to irrigated lands, residential areas and industries;
- consumptive use of water;
- water released from wastewater treatment plants;
- water returned to the environment;
- water used for power generation in hydropower plants.

Consumptive use of water is the part of withdrawn water that is evaporated, transpired by plants, incorporated into products or crops, consumed by humans or livestock, or otherwise removed from water environment. It is important to distinguish water withdrawals and water consumption. For example, a part of water extracted for irrigation and transported to farmlands is diverted and comes back to the hydrosphere, sometimes into the original water body. This part of water, after some delay, becomes available for further use.

Ground water is the most common and readily available source of fresh water on continents; it occurs near mountainous glaciers and ice caps, lakes, artificial reservoirs, wetlands, and rivers. Roughly 1,5 billion people depended on ground water as the source for drinking supply by the end of XX century. The amount of ground water withdrawn annually is estimated at 20% of global water withdrawals.

According to the United Nation Environment Programme, annual global freshwater withdrawal has grown from 3790 km³ (of which 61% was consumed) in 1995 to about 4430 km³ (of which 52% was consumed) in 2000. In 2000 about 57%

of the world's freshwater withdrawal and 70% of its consumption took place in Asia, where the largest world's irrigated farmlands are located [69]. Annual global water withdrawal is expected to be growing 10–12% every decade, increasing 1,38 times by 2025. Water consumption is expected to be growing at a rate of 1,33 times, with faster rates in Africa and South America (1,5–1,6 times), and the slowest increase in Europe and North America (1,2 times). The sectoral withdrawal of water is shown on the Table 1.2.

In most regions of the world, the annual withdrawal or use of water is a relatively small part (less than 20%) of the total annual internally renewable water resources. Nevertheless, in the areas suffering from water scarcity (Middle East and North Africa) this share amounts 73% of the total water resources.

Growing urbanization requires proper water supply and sanitation, which has become one of the main challenges for water industry worldwide. The megacities defined as the cities of more than 10 million inhabitants depend mostly on groundwater (in different degrees). Their total population will reach 9,6% of the world's urban population in the near future [70], with many people primarily in developing countries living in slums. This causes widespread water and environment contamination because of the lack of adequate drinking water supplies, sanitation, and proper sewage treatment.

In the mid-term future, agriculture will remain the major water user in developing countries. The level of water consumption will be increasing and influenced by climate changes, food self-sufficiency purposes, demographic development and economic factors.

Table 1.2

World use of water resources [50]

Country group	Total annual water withdrawal, million m ³	Agriculture %	Domestic %	Industry %
Sub-Saharan Africa	55	88	8	3
East Asia and Pacific	631	86	6	8
South Asia	569	94	2	3
Europe	110	46	14	42
Middle East and North Africa	202	89	6	5
Latin America and Caribbean	173	72	16	11
High income	893	39	14	47
World	3017	69	9	22

Ground water use in Europe. The principal source of freshwater in Europe is surface water; only about 30% of the total water withdrawn in the European Union

(EU) in the mid-1990s was ground water. However, in some EU countries (Austria, Denmark, Germany, Italy, Portugal, Switzerland) ground water remains the major source for public water supply, since it is readily available, commonly of high quality, and obtained at lower cost compared to treated surface water [12].

Total water withdrawals in northern, central, and eastern European countries decreased by 40% last decades, which is likely the result of droughts in recent years, and responding to them by advanced water management, reducing losses, recycling, using water more efficiently, and growing production of potable water in desalinization plants. The economic transformations in central and eastern European countries in 1990s had large effect on water use; it led to the decrease of water consumption for industrial purposes.

Ground water use in Ukraine. Total ground water reserves in Ukraine are estimated to exceed 20 km³ per year. They are distributed over the territory of Ukraine unevenly and form several basins. About 65% of country's ground water resources are concentrated in Dnieper-Donetsk and Volyn-Podilsk basins. Dnieper-Donets artesian basin in Central and Eastern Ukraine contains almost half (49%) of all ground water resources. Volyn-Podilsk artesian basin is located in north-western Ukraine. Fresh ground water occurs at the depth of 300 to 600 m in the northern regions of Ukraine and of 100 to 150 m in the south.

Water salinity increases from northern to southern regions reaching some g/L in the shallow aquifer, which makes this ground water impotable. Besides, due to extensive agricultural activities in southern regions of Ukraine and wide application of pesticides and fertilizers shallow ground water is contaminated in many areas.

The major user of water in Ukraine is industry (45% of the country's water consumption), and agriculture (about 40% of consumption) [18, 79]. Over the last decades water consumption decreased due to economic crisis but the specific water consumption is still exceeding the average world values and much more than this index in European Union. Water resources and water quality have been adversely affected by mining and industrial activities in South-Eastern areas and in Central Ukraine. Vast amount of toxic solid wastes (about 25 billion tons) accumulated in Ukraine is the biggest amount in Europe.

Hundreds millions of cubic meters of waste waters are discharged into surface water bodies, and retention ponds, which results in ground water salinization and quality deterioration. Local water resources in Donetsk coal basin were depleted due to mine drainage, the ground water level sank by several hundred meters in mining areas of Eastern Ukraine expanding on more than 8000 km². For this reason, the channel Dnipro-Donbas was constructed in 1970s to supply water and meet the local water needs in Eastern Ukraine. Dozens of mines have been already flooded completely or partially that has also adversely affected ground water quality.

Ground water systems have dramatically changed in Central Ukraine. Deep quarries and mines at deposits and tailings in Kryviy Rig iron ore basin have caused sinking of the ground water head up to 800 m and depletion of adjacent aquifers.

Last years the southern regions of Ukraine suffered from droughts increasing water demand and limiting the resources of water of drinking quality.

Ground water use in Africa. Average availability of water resources in Africa per capita is lower than the world average and exceeds only the same index in Asia. This is the result of a number of causes including

- a significant decline in the average rainfall since the late 1960s;
- the lowest runoff in the world (about 20%) due to high evaporation losses;
- high variability of supply due to extremely variable rainfall intensity, that is minimum in deserts (Sahara, Namibia) and maximum in western equatorial areas.

More than 75% of the African population, primarily in the North and South of Africa, use groundwater as the main source of potable water supply. Although ground water accounts for only 5% of the continent's total renewable water resources (in South Africa this index equals to 9%) ground water withdrawal in Africa is provided mainly from the non-renewable aquifer storage [67]. Therefore, the North African countries are considering desalinization as a promising tool to meet their growing water demands.

Ground water use in the USA. In fact, ground water is the supplementary source of water supply in the US [29], only about one fourth is the ground water share. Nevertheless, the percentage of ground water withdrawn for irrigation purposes continues to increase and reached 42% in 2000 instead of 23% in 1950. Most of ground water withdrawals occur in the arid western states, mainly in California, Texas, and Nebraska. The total population served by public and non-community water systems with ground water as the main source exceeds 100 million [78]

The share of ground water use for public supply increased from 26% in 1950 to 40% by the end of the XX-th century. Agriculture remains the major user of water in the USA, with more than 80% of the country's consumptive use. Last decade's droughts have seriously affected ground water resources in the central part of the continent, primarily in Great Plains, the multi-year average ground water levels have dropped in some areas by 2–3 m [34].

Ground water use in China and India. Water use in China has exceeded 550 km^3 in the beginning of the XXIth century [30]. Growing economy and population have caused serious water shortages in China over the past two decades; this trend was responded by the government plans to significantly reduce water consumption in agriculture and industry, being still 2-3 times more than the world average.

Ground water is the important source both for agriculture (40%) and for drinking water supplies (70%) [80]. Two thirds of available ground water are located in the south, and only one third of ground water resources is available in the semi-arid northern areas, where the major irrigated farmlands are located. This has led to dramatic ground water depletion in Northern China due to overexploitation estimated up to 2 km^3 per year in some provinces. The rate of sinking ground water level in deep freshwater aquifers is of 1 to 2 m/year; in some areas total depletion has already reached 100 m and more.

The total renewable ground water resources of India are estimated at 433 km³, whereas the volume of surface water is 690 km³ [43]. Agriculture remains the major consumer of water in the country; ground water is the source for irrigation on 57% irrigated lands, with small domestic farms being highly dependent on ground water for irrigation. About 70% of irrigation water and 80% of domestic supply come from ground water [63].

Regarding to the growing population and economic activities, there are threatening discrepancies between water demands, actual ground water withdrawal and the renewable ground water availability. There are also large differences among the regions of the country in surface and ground water availability and utilization. About 30% of ground water units are qualified as “non-safe” in terms of ground water exploitation. The latest governmental plans include the regulative measures, controlling drilling activities, promotion of artificial groundwater recharge, general education etc. Despite these efforts, the ground water industry of India is not being developed sustainably, as well as in many other Asian and African countries.

Ground water use in the Middle East and North Africa. This region is characterized by low precipitation and infiltration rates, prevalence of arid and semi-arid zones except some mountainous areas, comparatively big water reserves in so-called “fossil” aquifers formed thousands year ago, and growing demand due to increasing population density and pursuing the food security goals, all of those require larger water consumption for irrigation.

Most of the countries of this region except Tunisia and Morocco are overexploiting their renewable ground water resources. The total water withdrawal of water in these countries including Iran except Israel was 235,4 million m³ per year in 2000 [15] with almost 90% of this amount spent for irrigation, which is caused by extremely high evapotranspiration. Such countries as Saudi Arabia, Egypt, Libya, and Kuwait had the greatest water deficit in the region due to shortage in surface waters and rapidly growing demand.

Among the countries of this region six countries including Algeria, Egypt, Libya, Morocco, Tunisia, and Saudi Arabia are actively using “fossil” ground water resources [13]. This has led to significant sinking ground water levels reaching several dozens of meters in “fossil” aquifers in Arabian Peninsula and North Africa. Besides, growing demand and shortening non-renewable water reserves have enforced these countries to actively develop modern technologies for extensive production of potable water like sea water desalinization, which allowed mitigating water shortages, for example, in Saudi Arabia.

To reduce water consumption in agriculture the technologies of drip irrigation have been increasingly applied last years. Nevertheless, in the near future some countries will face the more severe water shortages (Oman, Yemen, Tunisia), which urgently needs the improvement of existing ground water management and rational use of the available resources.

Water scarcity can be defined as insufficiency of available resources to meet the demand on water. Annual water supply less than 1700 m³/year per capita means that the area is under water stress, if this value is less than 1000 m³/year per capita,

the population on this area suffers from water scarcity [69]. Thus, water scarcity depends not only on water resources, but also on its consumption and water quality.

Water scarcity may be temporary caused by natural (drought) or man-made factors (overexploitation, contamination occurred as a result of accidents or industrial activities). Agriculture is the sector of economy crucially dependent on water in most developing countries, and water scarcity threatens their food security. Extensive exploitation of fossil aquifers in the arid-climate countries has led to temporary increase in agriculture production followed by its drop, like it happened in Saudi Arabia from 1980s to the mid of 2000s. According to the UN forecast [69] by 2050 the number of countries facing water stress or scarcity could rise to 54, where there will be about 4 billion people or 40% of the estimated total population of the globe.

Water scarcity can be physical and economic. Physical scarcity begins if primary water supply exceeds 60% of potentially utilized water resources [44]. Countries with physical scarcity have to limit water consumption in agriculture and industry, import food and develop facilities for desalinization of sea water. Economic scarcity may appear even in the countries of sufficient water resources in case of rapid economic growth and demand on water. This type of scarcity can be prevented through additional storage and more efficient water management.

Climate change impacts on ground water. Increasing the mean world temperature during last decades has led to melting polar and mountainous ice, rise of the water level in oceans, more frequent droughts and natural disasters (floods, storms, tornado etc.). Extremes in precipitation have reduced the availability of surface runoff decreasing ground water recharge. Heat waves increase water consumption and put pressure both on surface and ground water resources. Warming of reservoirs increases water losses and affects the water quality due to algae blooms. Higher temperature causes water deficit in the topsoil and increases evapotranspiration sinking the water level in the shallow aquifer.

Rising water level in the oceans results in the displacement of fresh water in coastal aquifers with salt sea water, which deteriorates quality of water abstracted from coastal withdrawals. Regarding the fact that almost a half of the world's population lives in the coastal area this process may have large-scale after-effects on water supply in the world.

In the last decades droughts most adversely affected ground water resources on all continents. For example, the ground water level in shallow and artesian aquifers in central areas of the USA has irreversibly dropped by several meters after extremely hot summers in 2010 and 2012. Taking into account the total area of affected aquifers this means the loss of ground water reserves by hundreds of thousands of m³. The trend of sinking ground water has been also observed in other countries. In contrast, frequent floods in Central and Western Europe, and Eastern Asia resulted in high level of ground water.

Section review

1. Characterize world water resources.
2. Compare fresh water resources in surface water bodies with those in aquifers.
3. Characterize the layers of Earth's crust in terms of ground water reserves and availability.
4. Describe the reserves or sources of water that can be employed to meet the growing demand for water.
5. Characterize the major source of water supply in Europe, Ukraine, Asia, Africa, and the USA.
6. What were the causes of shrinking the Aral Sea and Lake Chad?
7. Characterize the purpose and essence of the TAWRW index.
8. What factors reduce the availability of surface and ground water?
9. Quantify the global potential water resources.
10. Characterize the major elements of water use.
11. What losses of water are associated with its use?
12. Characterize the current trends in global ground water withdrawal.
13. What are the differences in water use in European, African, and Asia countries?
14. Explain the term "water scarcity".
15. Specify local features of water use in Europe, the USA, China, India, the Middle East, North Africa, and Ukraine.
16. Characterize the recent trends in climate change and their impacts on ground water resources.

2. GROUND WATER FORMATION

2.1. Water in the Earth's crust

Forms of water in the Earth's crust. Ground water properties. Ground water zoning.

Forms of water in the Earth's crust. Water can be present in soils and rocks as free water, vapor, ice, and bound or attached water.

Free water can be capillary and gravitational water. *Capillary water* moves driven by capillary forces acting in narrow pores of rocks. Gravitational water is moved by hydrostatic pressure gradient under the influence of gravity. In the unsaturated zone water seeps down to the ground water level (ground water table), however, it can rise to the dried topsoil due to the difference in suction pressure.

Vapor occupies subsurface pores and cracks not filled completely with liquid water; it moves driven by the differences in vapor pressure or air flow. At low temperatures water retains in rocks in solid form as *ice*.

There are several kinds of attached (*bound*) water. Adsorbed water is retained by solid particles under the influence of forces generated by the interaction of water molecules with the particle surface and ion exchange. The rocks composed of fine mineral particles of high surface energy like clays contain a large amount of firmly attached water. This water is partially stored in clays even under high pressure and can be removed only at high temperature. Film water is retained weaker on the mineral particle surface.

Chemically bound water is enclosed in the crystal lattice of some minerals. Crystallization water is part of the crystal lattice in the form of H₂O molecules. Water in minerals in the form of hydroxyl or hydrogen ions can be removed only in case of destruction of the mineral compound molecule under high temperature. The dehydration temperature for some of these minerals exceeds 1000 °C.

Ground water properties. Physical properties of water differ from those of most natural compounds. When melting water does not expand like almost all other substances, in contrast it contracts. Water density increases as temperature increases from 0 to 4 °C, and begins to decrease at higher temperatures. Water has extremely high values of specific heat capacity, latent heat of melting and boiling. All specific properties of water are due to the features of water molecule structure and the nature of intermolecular bonds.

Physical properties of ground water depend on water type, composition and concentration of dissolved solids, temperature, and pressure. Ground water density varies from nearly 1 g/cm³ for fresh water to 1,3–1,4 g/cm³ for extremely saline water (brines). The temperature and pressure increase with depth. On average, temperature grows by 3 °C for every 100 meters down. The hydrostatic pressure of ground water increases by 1 atm for every 10 m of depth, for more dense brines this gradient is higher.

An increase in temperature leads to a decrease in ground water density (Fig. 2.1,a). Fresh water density at 100 °C equals 0,958 g/cm³, and at 250 °C it falls to 0,799 g/cm³ (Fig. 2.1,b). Increasing pressure results in greater water density. Fresh water compressibility equals to $5 \cdot 10^{-5} \text{ atm}^{-1}$. This means, for example, that at the pressure of 200 atm water is compressed by 1%, with increasing its density. Such pressure can be put by the weight of a rock layer of approximate thickness 750 m and density 2700 kg/m³. Elastic properties of water are highly important for deep ground water hydraulics. An increase in temperature leads to a significant decrease in water viscosity, which facilitates seepage through small pores and cracks.

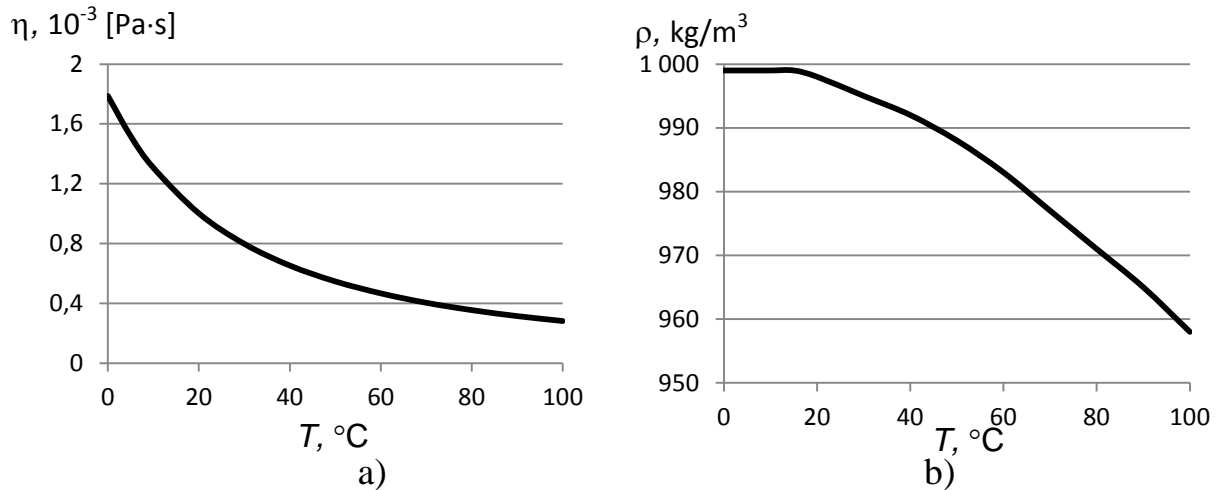


Fig. 2.1. Dynamic viscosity (a) and density (b) of water versus temperature T .

Physical properties of attached water differ significantly from those of free ground water. Depending on rock or soil saturation the density of adsorbed water can reach 2 g/cm³. Transformation of such water into free water results in essential volume increase. Firmly attached water has higher viscosity; its freezing temperature is -78°C .

The critical temperature for fresh water is 374°C , and for water solutions it reaches $400 - 450^\circ\text{C}$. Under so-called supercritical conditions—at a temperature of more than 374°C for fresh water and more than 425°C for saturated solutions, and a pressure of 218 atm—water occurs in a special state without differences between steam and fluid. In fact, the physical properties of liquid water and steam do not differ above that point. The water in such state has lower density and viscosity than liquid water, which increases migrating mobility of water in deep rocks.

Thus, growing temperature in the crust results in forming more water vapor in deep layers due to evaporation. At some depths all water converts into the mixture of steam and water. This is a kind of water plasma because water molecules move at the velocity of gas molecules, and mixture density is close to liquid water density.

The data on water occurrences in deep strata are very poor. The deepest borehole in the world drilled in Kola Peninsula has reached a depth of only 12 km [9]. Due to the lack of data the estimates of water reserves at this depth vary significantly. Usually the calculations of water storage account for the rock top strata

of thickness of 2–3 km, sometimes 5 km. Deep drilling boreholes have revealed the fact that ground water can exist in the liquid form far below 5 km the surface, and somewhere, depending on geologic conditions, even deeper than 10 km.

As a result of contacting with various rocks, seeping ground water enriches with many chemical compounds, therefore, ground water is actually the natural complex solution containing ions, molecules of various salts, colloids, and gases.

Ground water zoning. Ground water forms a variety of aquifers considered as basic hydrogeological units (See also Section 3.1). The simplest aquifer is a porous or fractured reservoir filled with water and confined by one or two low-permeable waterproof layers. These aquifers often form interconnected complex systems of different scales in size and depth of water occurrence.

There are three large zones in the Earth's crust vertical section distinguished by the exchange intensity with other hydrosphere components, mostly from surface water bodies [10, 20].

1. The *zone of active ground water circulation* is situated below the ground surface down to the depth of 0,3–0,5 km and includes perched, shallow and some artesian aquifers. Water in this zone is actively exchanged with surface water bodies (rivers, lakes, wetlands, seas, and oceans). Ground water velocity is relatively high and may reach some centimeters per second. On average, a complete cycle of exchange with surface waters lasts for some decades or centuries.

2. The *zone of slow ground water circulation* lies below the active circulation zone above the depth of 1.5–2 km. Water flows in this zone much slower due to decreased fracturing and porosity. Because of impeded exchange with surface water bodies the average time of water replacement reaches dozens of thousands of years.

3. The *zone of passive ground water circulation* is located below the depth of 2 km. The estimated time of ground water renovation is millions of years, which enables long-term storage of “fossil” water in ancient sea water basins.

Thermal water occurrences get more frequent with increasing depth. However, this pattern is often disturbed by the abnormalities caused by climatic factors, geological and tectonic features, and active volcanism. Dynamics, composition, and water circulation rate depend on the features of geological structures as well as ground water basins, geological development of these structures, water origin and local circulation time.

Huge aquifer systems and basins have been discovered even in most arid and deserted areas of the world. It was found out that fresh water reserves in dry steppe and desert areas of Kazakhstan, North Africa, and Arabian Peninsula are comparable to the volumes of water stored in Lake Balkhash or Aral Sea (before extensive irrigation since 1970s). Fresh water aquifers in Turkmenistan can produce more than 400 thousand m³ of water per year. Ten big ground water basins have been revealed in Sahara that is the world largest desert. Very often these basins are found in the areas of marine sedimentary rock occurrence. Alternating permeable and low-impermeable layers is characteristic for these areas.

The ground water in the upper layers of the Earth's crust can be classified according to Pinneker [17] (Table 2.1).

Table 2.1

Ground water classification according to water occurrences [17]

Group	Sub-group	Type (of aquifer)	Class	Sub-class		Specific conditions	
				Water in porous aquifers	Water in fractured and karst aquifers	Water on the permafrost territory	Water in the areas of modern volcanism
Ground water on lands	Ground water of unsaturated zone	Perched	Perched (in various sense)	Soil and perched water		Active layer	Upper layer of lava cover
	Ground water of saturated zone on lands	Mostly unconfined	Shallow ground water	Upper aquifer on the regional aquitard	Upper zone of the intensive fracturing and karst	Above, inter, and inside permafrost	Upper layer of lava cover
			Artesian water	Interlayer water under hydrostatic pressure	Deep zones of fracturing under hydrostatic pressure	Below permafrost	Hydrothermal systems under hydrostatic pressure
		Confined	Deep water	Deposits under geostatic pressure and endogen forces	Deep fissures influenced by endogen forces	Absent	Volcanic and hydrothermal systems associated with magma
				Shelf and marine deposits	Karstified rocks on shelf and faults	Below the permafrost in polar seas	Submarine volcanic and ocean hydrothermal systems
			Water not associated with lands	Deposits in deep water depressions	Surge channels and rifts in the ocean bottom	Absent	
Ground water below seas and ocean	Ground water in the submarine saturated zone	Mostly confined					

2.2. Geologic characterization of ground water origin

Ground water origins. Infiltration water. Sedimentary water. Juvenile water. Igneous water.

Ground water origins. Ground water is the part of the lithosphere; therefore, their origins are closely related to the formation of rocks and minerals. Because of its mobility water can relatively quickly, in a geologic time scale, move subsurface in different zones of the Earth's crust and be involved in various geological processes.

Ground water has been formed

- in the areas of magma movement and volcanic activities,
- from the ocean water during sea digression,
- as a result of sea water intrusion in coastal aquifers,
- from surface water inflows including rain, snow, seepage from rivers, lakes, wetlands, and melting glacial ice.

The main types of ground water distinguished by the origin are infiltration water, sedimentary water, igneous water, and juvenile water [10].

Infiltration water originates primarily from precipitation or melting snow seeping through soils or rocks (Fig. 2.2,a). Another source of infiltration water is the surface water in flood-plains leaking downward during and after river floods. Infiltration water is widespread in upper layers of the Earth where the intensive water exchange occurs. In the zone of slow water exchange, commonly at significant depths, one can find stored fossil water of infiltration origin.

Sedimentary water originates from deposition of marine sediments (Fig. 2.2,b). The water content of sea mud in bottom layers of deposits reaches 80 % [SD]. Due to condensation as a result of dipping under the weight of sediments the mud releases some amount of water. Sedimentary water evolution is closely related to the transformation of marine sediments into rocks, which is also called "sediment lithification". This process has changed not only mineralogical composition of sediments, but also the chemical content of water interacting with solids. Therefore, the chemical composition of sedimentary water may often notably differ from the initial sea water composition.

Fossil sedimentary water is stored in rocks after sea digression under the conditions of slow water exchange unless this water was replaced with infiltration water. Sedimentary water often occurs in continents far from the coast where ancient sea basins were formed.

Infiltration and sedimentary water comprise the most part of ground water stored in the upper Earth's layers. The proportions between these types of water depend on geological development of the area, hydrogeological features, and water exchange rate. Actually, the proportion between infiltration water and sedimentary water is the result of rainfall infiltration and water release from condensing clay layers.

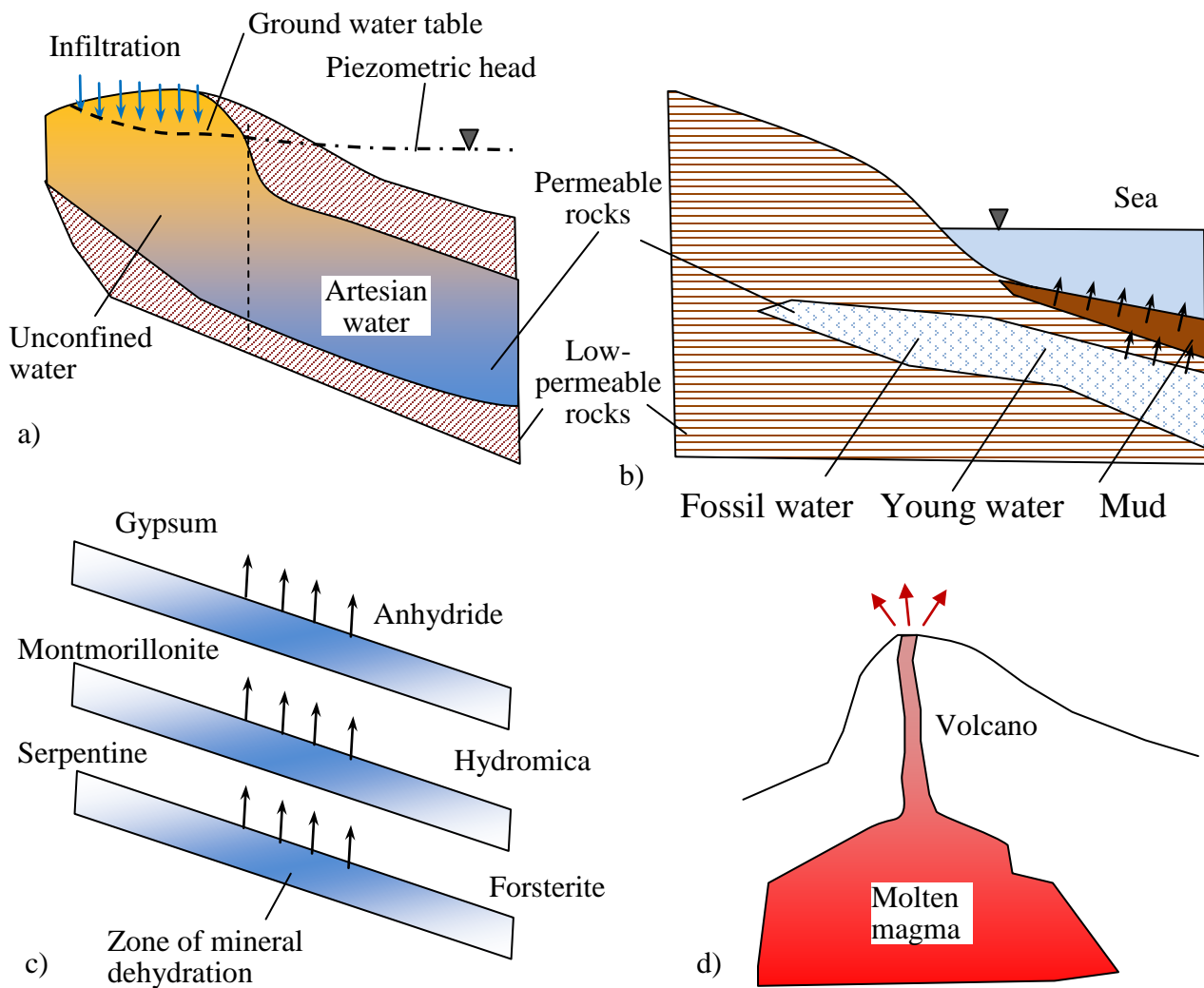


Fig. 2.2. Genetic types of ground water [10]:

a) infiltration water, b) sedimentation water, c) juvenile water, d) igneous water.

The first process takes place on continents where *meteoric water* derived from precipitation entering the soil and rocks is gradually replacing the water of sedimentary or other origin. Under relatively intensive water exchange this may result in full displacement of antecedent water by infiltration water.

Compaction of silts and clays is accompanied with exudation of sedimentary water, which plays the key role in marine sedimentation. However, this process can occur also on continents after sea digression. Rising water expelled from compacted mudstones displaces infiltration water. Such kind of water exchange is actively developing in the deep zones of geologically young deflections. Interaction between infiltration water and sedimentary water influences the chemical composition of deep ground water that is often formed by mixing of these types of waters.

Juvenile water is formed under the impact of high temperature on the water-bearing minerals, for example, as a result of degasification of mantle material in the course of metamorphism and magmatism. Having reached the crust this water mixes

with ambient water of other origin. An increased content of CO₂, He, and O₂ could be an indicator of juvenile water.

Chemically bound (attached) water transforms to free water (Fig. 2.2,c). The process causing water exudation occurs in various thermodynamic zones of the crust. Even at temperatures of 80–90 °C gypsum begins to dehydrate and converts into an anhydrous mineral. Each ton of gypsum (CaSO₄·2H₂O) fully converted into anhydrite (CaSO₄) releases about 210 kg of water. Gypsum also dehydrates under increased pressure because it has much larger volume than anhydrite.

According to experimental studies [33] clay minerals like montmorillonite of 12–24 % water content are converted to hydromica that contains usually 10 % of water at the depth of 2 to 6 km depending on temperature and pressure. As a result, a large volume of so-called interlayer water enclosed in the crystal lattice of montmorillonite is released. Serpentine contains about 13 % of water; it dehydrates in deep rocks at high temperature, which is also characteristic for other minerals with attached water.

Exudation of attached water contained in minerals is the result of metamorphism of rocks submerging into the high-temperature zone. Released water rises to the surface and is involved in geological development near the ground surface.

Igneous water originates as a result of water exudation from magma (Fig. 2.2,d). The experiments [32] have shown that molten magma is capable of dissolving and assimilating water at high pressure and releasing it with falling pressure. Thus, magma at great depths absorbs water from surrounding rocks. In course of rising through the volcanic channel at falling pressure magma releases the excess of water. Vast quantities of gases released during volcanic eruptions are known to contain high percentage of water vapor.

The mass water content in the basalt magmatic melt ranges from 1 to 2 %. However, water solubility in the melt is much higher, which means possible melt enrichment with water in this way. Indeed, the amount of attached water in some igneous rocks formed under high pressures at great depths reaches of 4 to 5 %.

According to some estimates [2] heat release in active geologic hydrothermal systems in volcanic areas is extremely high and cannot be explained only by cooling magma material. A stable thermal regime of hydrothermal systems may be linked with the movement of water-bearing magma releasing endogenous steam or liquid water.

Thus, igneous water can be heterogeneous by origin. Along with the water initially enclosed in rocks magma can absorb water of infiltration or sedimentary genesis from surrounding rocks or juvenile water released as a result of mineral dehydration.

2.3 Hydrological cycle

Global water circulation. Water balance. Example of water balance calculation. Main elements of the hydrologic cycle.

Global water circulation. The hydrologic cycle comprises water circulation on the Earth from oceans to the atmosphere, then to land and back to oceans. The main pathways of the hydrologic cycle are shown in Fig. 2.3. Water evaporated from oceans, lakes, and rivers is carried by wind in the atmosphere and eventually falls as rain or snow onto the land, oceans, rivers, and lakes. Water fallen onto the land partially evaporates, quickly or slowly depending on climate, it partially flows into streams or lakes as surface runoff, and the rest of water infiltrates into soil and recharges ground water. Some of soil water is transpired back to the atmosphere by plants; the remaining water flows subsurface and discharges to surface water.

Subsurface water is present in the soil-water zone just below the ground surface, in the unsaturated zone (vadose zone) and saturated zone (phreatic zone). Apart from primary pores the soil-water zone contains voids formed by cracking and plant root decay. These voids enhance infiltration which is defined as downward percolation of precipitation water.

Pores in both the soil-water zone and unsaturated zone are filled with water solution and air. In the saturated zone all pores are almost completely filled with water solution, however, pore space contains a small portion of dissolved or squeezed gas. The saturated and unsaturated zones are separated by an imaginary surface called the water table or water level. Generally, ground water refers to water that occurs in the saturated zone, but water and vapor movements in the unsaturated zone are also studied by hydrogeology.

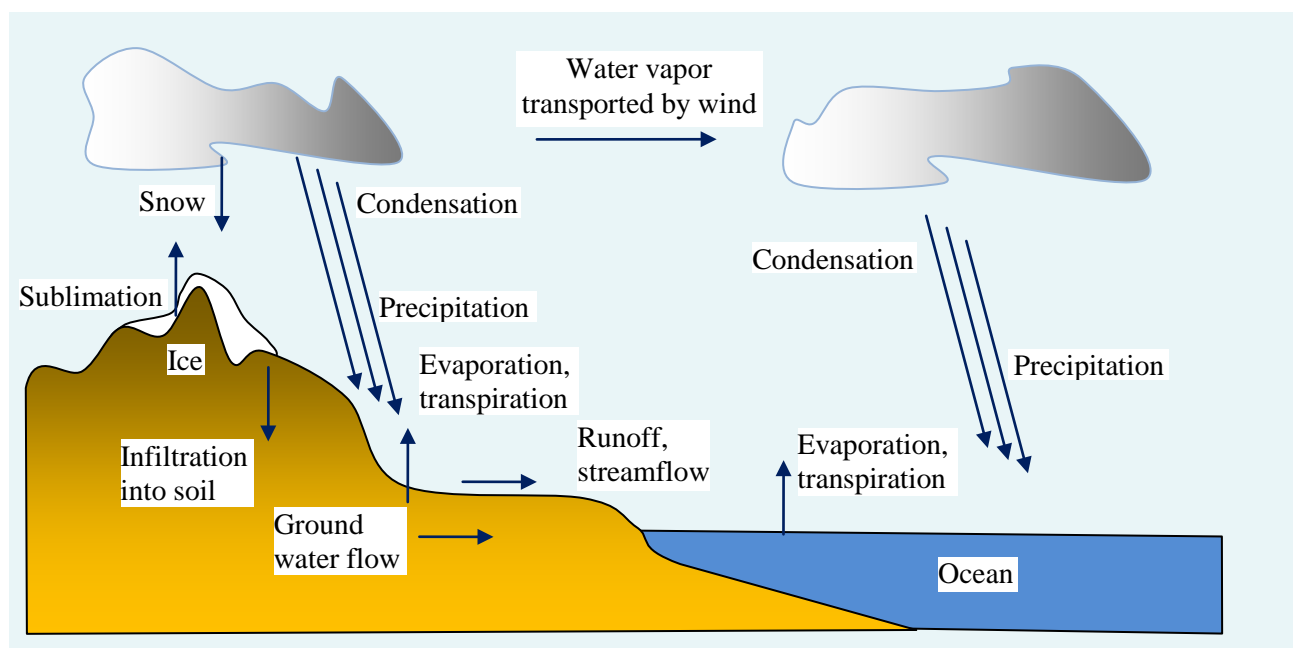


Fig. 2.3. Scheme of the hydrological cycle [8]

Water balance. For each of subsurface domain one can account for all water constituents with the principle of mass conservation

$$\text{Input} - \text{Output} = \text{Change of storage.}$$

The term *conservation* means no loss or gaining water moving in the hydrologic cycle. This principle is applicable both to a global and a basin scale. On the global scale, the water balance equation can be applied to one or three domains including atmosphere, land (on-ground and underground), and oceans. A simple balance equation is written as

$$P - E - Tr - R_o = \Delta S \quad (2.1)$$

where P is precipitation on land, E is evaporation from the land surface, Tr is transpiration from the land by plants, R_o is the total outflow from land to oceans, and ΔS is the change of water storage on and under the ground surface.

In many applications it is important to calculate water balance for a domain of smaller scale, comparable to a regional or local ground water system (ground water basin). Reducing the scale complicates the problem because of more details to be adequately taken into account. Thus, the water balance equation for some specific domains (mountainous, desert, and coastal) may include different input and output components. Also, some components can be either sinks or sources depending on local hydrogeological features. Much of water discharges into surface streams, however, *losing streams* recharge the ground water system by leakage through beds. Alternatively, *gaining streams* receive water discharged by ground water, mainly from downstream parts of ground water basins.

On the basin scale, the ground water balance equation can be written as

$$R_N + Q_{swi} - E - Tr - Q_{gwo} - Q_p + Q_{gwi} = \Delta S \quad (2.2)$$

where R_N is the recharge to ground water, Q_{swi} is surface water inflow to ground water storage, E is evaporation, Tr is transpiration, Q_{gwo} is outflow from ground water storage to surface water, Q_p is the total pumping rate for the basin, Q_{gwi} is the ground water inflow to the basin from other adjacent hydrogeological basins, ΔS is the change in ground water storage within the basin.

Example of water balance calculation. Calculate the subsurface runoff from a hydrogeological basin; estimate the change in runoff in case of increasing precipitation or evapotranspiration.

Assume the total basin area $A = 30 \text{ km}^2$, mean precipitation is $\varepsilon = 500 \text{ mm/year}$; the annual evaporation and transpiration rates from the ground water table are $e_a = 50 \text{ mm}$ and $t_a = 10 \text{ mm}$ correspondingly. Ground water withdrawal for domestic supply makes $Q_p = 200 \text{ m}^3/\text{day}$ or $730000 \text{ m}^3/\text{year} = 7.3 \cdot 10^5 \text{ m}^3/\text{year}$.

There is only one river within the basin and surface water inflow to ground water storage is $Q_{swi} = 7 \cdot 10^5 \text{ m}^3/\text{year}$; outflow from ground water storage to surface water bodies is estimated at $Q_{gwo} = 1 \cdot 10^6 \text{ m}^3/\text{year}$.

The recharge to ground water R_N is calculated as the infiltration rate w multiplied by the total basin area A . For this evaluated basin infiltration can be assumed as 20% of precipitation, thus,

$$w = 0,2 \cdot \varepsilon = 0,1 \text{ m/year.}$$

Therefore,

$$R_N = w \cdot A = 0,1 \text{ m/year} \cdot 30 \cdot 10^6 \text{ m}^2 = 3 \cdot 10^6 \text{ m}^3/\text{year.}$$

Total evapotranspiration equals the sum of evaporation and transpiration rates multiplied by the basin area, therefore,

$$E + Tr = (0,05 + 0,01) \cdot 30 \cdot 10^6 \text{ m}^2 = 1,8 \cdot 10^6 \text{ m}^3/\text{year.}$$

Assume steady-state hydrogeological conditions. Substituting $\Delta S = 0$ in Eq. 2.2 yields

$$\begin{aligned} Q_{gwi} &= -R_N - Q_{swi} + E + Tr + Q_{gwo} + Q_p = \\ &= (-3 \cdot 10^6 - 5 \cdot 10^5 + 1,8 \cdot 10^6 + 8 \cdot 10^5 + 7,3 \cdot 10^5) \text{ m}^3/\text{year} = 3,0 \cdot 10^4 \text{ m}^3/\text{year.} \end{aligned}$$

Therefore, the inflow to the basin equals to $3,0 \cdot 10^4 \text{ m}^3/\text{year}$. This means a small shortage of water, or about 3% of withdrawn water.

In case of increased climate humidity or growth of precipitation (let it be 10% increase) at the same evapotranspiration the ground water recharge also increases

$$w = 0,2 \cdot \varepsilon \cdot 1,10 = 0,11 \text{ m/year, which yields } R_N = 3,3 \cdot 10^6 \text{ m}^3/\text{year.}$$

Substituting this value into Eq. 2.2 results in $Q_{gwi} = -2,6 \cdot 10^5 \text{ m}^3/\text{year}$. This means that there will be an excess of water in the basin, and the estimated outflow from the basin will be $2,6 \cdot 10^5 \text{ m}^3/\text{year}$.

Consider another case of drier and hotter climate. Let precipitation diminishes by 10% and evapotranspiration will be higher by 10%. Then,

$$w = 0,2 \cdot \varepsilon \cdot 0,90 = 0,09 \text{ m/year, which yields } R_N = 2,7 \cdot 10^6 \text{ m}^3/\text{year.}$$

$$E + Tr = 1,10 \cdot (0,05 + 0,01) \cdot 30 \cdot 10^6 \text{ m}^2 = 2,16 \cdot 10^6 \text{ m}^3/\text{year.}$$

Substituting these values into Eq. 2.2 results in $Q_{gwi} = 3,9 \cdot 10^5 \text{ m}^3/\text{year}$. This means higher water shortage reaching 53% of withdrawn ground water.

Exercise. Following the example above calculate the change in ground water storage in case of increase in precipitation

#	ε , mm/year	e_a , mm/year	t_a , mm/year	Q_{swi} , m^3/year	Q_o , m^3/year	Q_p , m^3/day
1	450	50	10	$7 \cdot 10^5$	$1 \cdot 10^6$	200
2	500	40	15	$6 \cdot 10^5$	$9 \cdot 10^5$	250
3	600	60	5	$8 \cdot 10^5$	$1 \cdot 10^6$	150
4	650	70	15	$1 \cdot 10^4$	$1,2 \cdot 10^6$	250
5	700	80	25	$2 \cdot 10^4$	$1,5 \cdot 10^6$	350

The main elements of the hydrological cycle are precipitation, evaporation, evapotranspiration, infiltration, overland flow, interflow, and streamflow. These components are united in a basin hydrologic cycle as shown in Fig. 2.4.

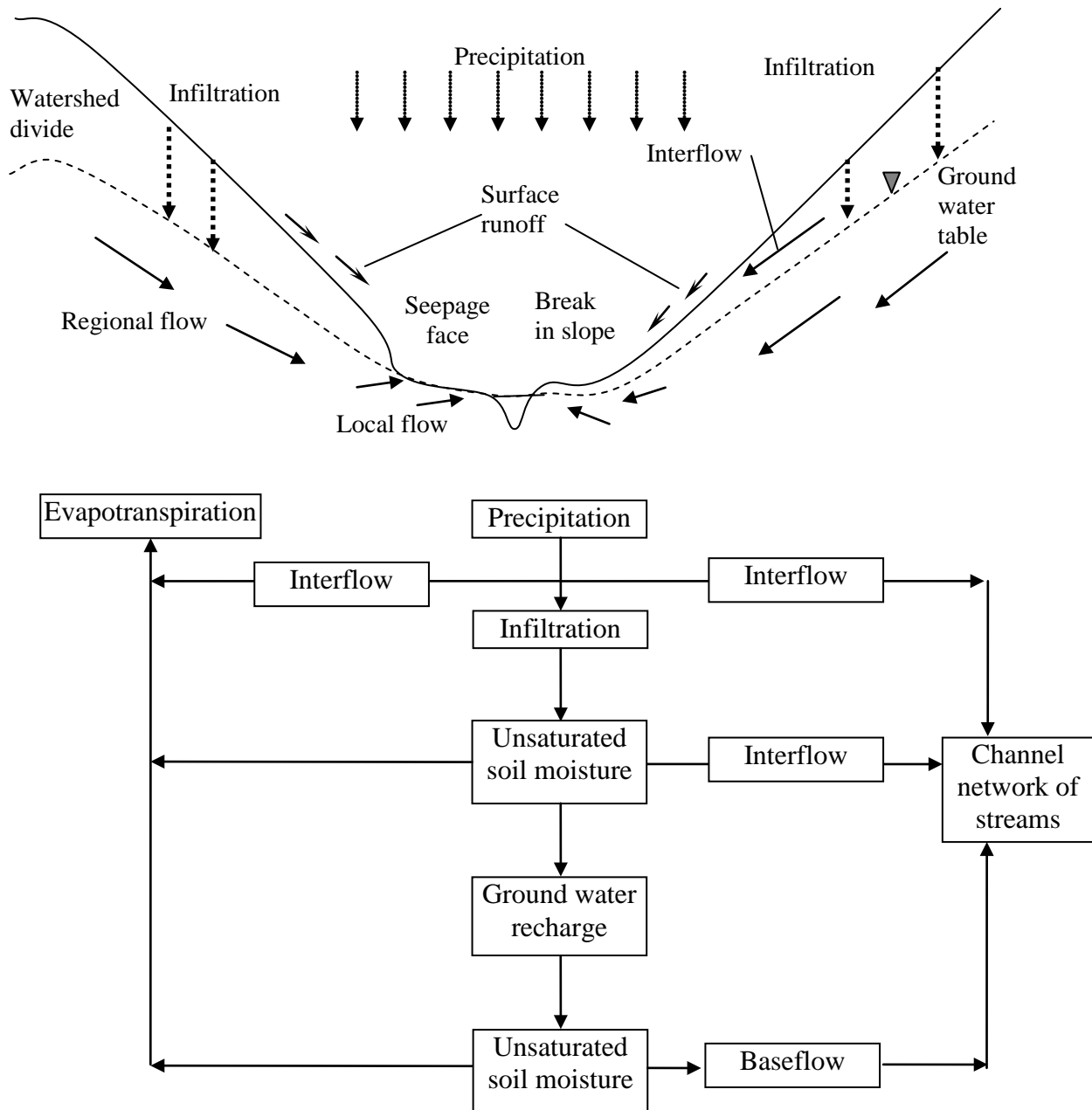


Fig. 2.4. The basin hydrological cycle [8]

Precipitation includes various forms of water falling to the ground from the atmosphere. Precipitation can occur as rain, snow, drizzle, hail, sleet, and ice crystals. It can be measured by a number of devices; the simplest are containers collecting precipitation during the rainfall. The modern precipitation containers (gages) have the capability to record the time, duration, and intensity of precipitation, then store and transmit this information electronically.

The accuracy of precipitation measurements is affected by weather disturbances (strong wind during storm), and small amounts of dew and rime

included in the total measured precipitation. The gages underestimate the actual precipitation, particularly at strong wind.

Many applications need the precipitation data estimated over relatively large areas. The simplest approach is to calculate the average of precipitation measured at weather stations. There are more sophisticated methods giving the figures closer to the reality. One of them is the Thiessen-weighted average that assumes the precipitation data are the most representative for the areas surrounding the points of measurement [64]. New radar-based advanced techniques have provided much more exact estimation of the precipitation spatial distribution. For each rain or storm occurrence the strength of reflected radar signal is proportional to the precipitation rate. Such technique is now rapidly implemented, most actively in the USA.

Evaporation is the process of transforming a liquid to a gas (water to vapor). In hydrologic application the term *evaporation* means the quantity of water lost from the soil or water surfaces (rivers, lakes, wetland, and oceans). A number of methods are developed and applicable to estimate or measure the rate or amount of evaporation. Its value depends on solar radiation, temperature, wind velocity, air humidity, soil water content etc. Evaporation from plants is called *transpiration*, thus, the combined process of evaporation and transpiration is called *evapotranspiration*.

Evaporation reaches the maximum for a water surface; it is much lower for the soil surface, usually unsaturated. Potential evaporation is much higher than actual evaporation from the soil surface because of forming the upper drying topsoil “cover” that inhibits evaporation from deeper soil layers. *Potential evapotranspiration* is defined as the amount of water that would evaporate or transpire if sufficient water was available in the soil to meet the demand. In arid areas the actual evaporation and evapotranspiration are much less than their potential rates.

In the field, evapotranspiration is measured by lysimeters that are soil-filled tanks where plants are grown. Accurate weighting lysimeters and measuring water added to the lysimeters enables proper estimating evapotranspiration rates.

There are also a variety of empirical methods to evaluate the potential evapotranspiration rate, depending on the temperature of air [65]. A simple empirical formula to estimate annual evaporation from the ground water surface was also derived by F. Averianov [1]. In case of high elevation of the ground water table near the soil surface the evaporation rate E (mm/year) is calculated as follows

$$\varepsilon = \varepsilon_0 \left(1 - \frac{H}{H_{cr}} \right)^n, \quad (2.3)$$

where ε_0 is evaporation rate from the water surface, mm/year; H is the ground water depth; H_{cr} is the critical depth of ground water level, n is the factor depending on soil properties. If the ground water level is below the critical depth H_{cr} , no evaporation is assumed to occur. The empirical factor n ranges from 1 to 3; the critical depth H_{cr} ranges from 120 cm for temperate climate to 400 cm for arid zones.

Example. Calculate how much the evaporation rate increased if the ground water level H rose from 1,5 m to 1 m below the soil surface, assuming the critical depth of ground water level $H_{cr} = 2$ m, the evaporation rate $E_0 = 700$ mm/year; and the empirical parameter $n = 2$.

Substituting these parameters into the Eq. 2.3 yields the actual evaporation $E = 175$ mm/year for $H = 1$ m and $E = 43,8$ mm/year for $H = 1,5$ m. Thus, evaporation increased by four times in case of higher elevation of ground water table.

Infiltration is the process of downward water seepage through the soil. The infiltration rate depends on near surface conditions and available water content. The maximum infiltration rate decreases in time. When water initially falls to the soil surface, the infiltration rate is equal to the discharge of water coming into the soil. If water infiltrates completely, there will be no overland flow. If water is continuing to be added, ponds and puddles are formed in the local depressions of the soil surface.

Once forming of ponds begins, the infiltration rate is strongly dependent on hydraulic properties of the topsoil. Infiltration from free water bodies on the ground surface is called *ponded infiltration*. Its rate is commonly decreases with time because of deeper wetting of the soil. After long wetting under ponded conditions, the infiltration rate tends to be constant. The rate of the steady-state infiltration can be estimated by hydraulic conductivity of the upper soil layers within a depth from 0,5 to 1,0 m below the ground surface.

Almost always infiltration rate is non-zero even in deserts, where small recharge is formed as a result of a few strong rains during a year. In temperate climate infiltration may reach the half of precipitation depending on the relief and soil properties that facilitate or prevent from surface runoff.

Overland flow or surface runoff is followed by ponding. *Overland flow* is flow across the land surface to a nearest channel. Another pathway for storm water to streams is *interflow*; this is a lateral flow of water above the water table during storms. Interflow can be directed to a lake or a stream, or it can appear locally at the ground surface. Overland flow and interflow can be grouped together as *direct runoff*.

A *watershed* or *basin* bounds the area that contributes surface runoff to some systems or stream channels. The watershed area can be contoured using topographic maps, which are now often available in digital form. The boundary between adjacent watersheds or basins is called surface water divide, which is often, but not always, the divide between ground-water basins.

Surface runoff can be estimated by various methods. One of them [77] is applicable to small basins of up to some dozens of hectares. According to this method the peak discharge Q is proportional to the average rainfall intensity w and the drainage area A

$$Q = C w A, \quad (2.4)$$

where C is the empirical runoff coefficient depending on the land use type.

Streamflow. Streams and rivers return surface runoff, interflow, and ground water recharge in the hydrologic cycle and divert these waters to the oceans. Discharge of a stream or river is the volume of water flowing per time unit, measured in m^3/s in SI System. Quantitatively, this parameter is usually presented by discharge hydrograph as the function of time.

Stream discharge Q_s can be approximately calculated as the product of streamflow velocity v_s and the area of stream cross-section A_s (Fig. 2.5) [59].

$$Q_s = v_s A_s. \quad (2.5)$$

In real streams velocity varies within the stream, therefore, one should subdivide the stream cross section into smaller cross-sections and estimate discharges through each segment using the formula similar to Eq. 2.5. The total discharge is the sum of discharges coming through all segments.

The average velocity in each vertical section is determined by averaging values in the points at 0,2 and 0,8 of the stream depth; in a shallow water near shore a single measurement is sufficient at a 0,6 depth. The vertical sections are divided in such a way that maximally 10% of the flow comes through each.

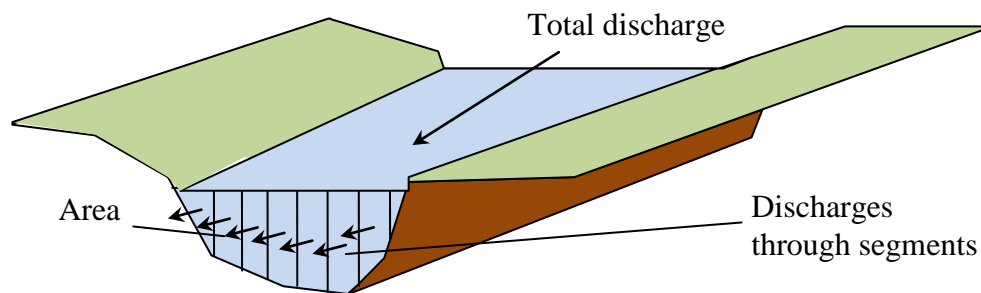


Fig. 2.5. Scheme to streamflow calculation

Section review

1. Describe the forms of water occurrence in soils and rocks.
2. Which soils have the maximum content of chemically bound water? Why?
3. Can soils or rocks be fully saturated with the fluid(s) and contain no gas? Why?
4. Describe the ranges of ground water density depending on pressure, salinity, and temperature?
5. What is the cause of the geothermal gradient?
6. Give a quantitative assessment of elastic properties of water.
7. Describe water occurrences at the depths below 500 m.
8. Characterize features and rates of water circulation at different depths.
9. Evaluate water reserves in subsurface reservoirs found in arid zones.
10. Compare ground water forms in shallow aquifers and deep strata using Pinneker's classification.
11. Characterize major forms of ground water according to Pinneker's classification.
12. What are the main origins of ground water?
13. Compare infiltration water and sedimentation water by origin, age, and occurrences.
14. Describe the role of compacting sediments in ground water formation.

15. Analyze the differences and similarities between juvenile and meteoric water.
16. Give the examples of chemically attached (bound) water.
17. Quantify the water content in igneous rocks and other sediments.
18. Characterize the major water pathways of the global hydrological cycle.
19. Describe the major elements of water balance.
20. Explain the principle of water mass conservation giving an example.
21. Describe the terms “evaporation” and “evapotranspiration”.
22. Why does actual evaporation differ from potential evaporation?
23. Explain the time patterns of ponded infiltration as the form of vertical percolation.
24. How can we estimate surface runoff and streamflow?
25. Can the surface water divide be different from the divide between ground-water basins?

3. AQUIFERS

3.1. Ground water system

Hydrogeological units. Hydrogeological structures. Key elements and geometry of ground water systems.

Hydrogeological units are the elements of the ground water system [37] (Fig. 3.1). Aquifer is the primary unit in ground water investigations. *Aquifer* is defined as a lithologic unit or a combination of lithologic units capable of yielding water to pumping wells or springs. An aquifer can be comparable by extensions with a group of geological formations or a part of a formation. It also may be located independently of any geologic unit. Units of low permeable material bounding an aquifer are called *confining beds*.

Definition of an aquifer as the source for water supply can make confusion. A low-permeable unit might be considered as a confining bed in water-abundant areas. In contrast, a deposit of the same permeability could be considered as an aquifer in the areas of water scarcity. In actual field studies the ambiguity in the term “aquifer” does not pose the problem because its properties explicitly define the hydraulic type of a studied unit.

The *water table* forms the upper boundary of *unconfined aquifers*. When shallow wells or piezometers are installed into the unconfined aquifer, the water levels in these wells are approximately equal to the water table position.

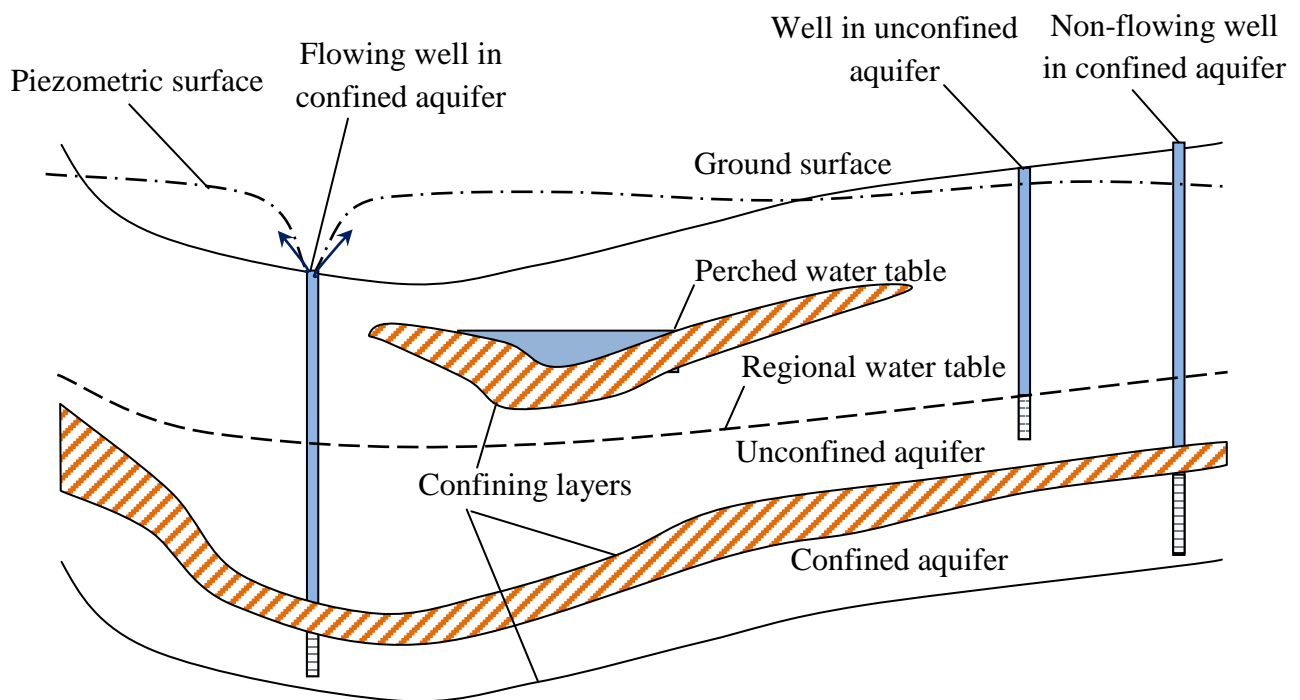


Fig. 3.1 Schematization of aquifers (taking into account [72])

A *confined* or *artesian aquifer* is bounded above and below by low-permeable units (confining beds); in other words, the upper and lower boundaries of the confined aquifer are confining beds. The water level of a well or piezometers installed in the confined aquifer commonly positions somewhere above its upper boundary. In some cases the water level of a well occurs above the ground surface; such a well is called a flowing artesian well. A contoured map of hydraulic heads for a large number of wells in the same aquifer forms a potentiometric surface.

A *perched aquifer* is a specific case of an unconfined aquifer that develops above the regional water table. Actually, the perched aquifer is the saturated “island” in the unsaturated zone because this aquifer is “isolated” within the unsaturated zone.

The terms *aquifuge*, *aquitard*, and *aquiclude* are used in hydrogeological literature applied to various types of confining beds. Sometimes the terms *aquifuge* and *aquiclude* are encountered but replaced with more general term *confining bed (layer)*. An *aquifuge* is the ultimate low-permeable hydrogeological unit, which is almost impermeable. An *aquitard* is a low-permeable unit that is capable to store and transmit water between adjacent aquifers, but at a much slower rate than an aquifer; it cannot provide significant amounts of potable ground water to wells or springs. The stored and transmitted water is available to pumping wells in nearby aquifers. The term *aquiclude* is the synonym for confining bed. The term *semi-confining* bed refers to a leaky aquitard.

Hydrogeological structures. *Hydrogeological structure* is the term to define recharge and discharge zones of a ground water system. The basic types of hydrogeological structures are shown in Fig. 3.2 [36, 37]

1. *Open hydrogeological structure.* Recharge and discharge zones are fully defined; recharge takes place over the entire area of the system or aquifer directly exposed to the ground surface. Discharge of the system is either at the contact with the impermeable base (Fig. 3.2,a) or along a main basis of erosion such as a large permanent river or coastal line (Fig. 3.2,b).
2. *Semi-open hydrogeological structure.* The discharge zone is fully defined; the ground water system is partially isolated from the ground surface by low-permeable or impermeable cover. The recharge zones are mostly or partially known (Fig. 3.2,a or Fig. 3.2,b).
3. *Semi-closed hydrogeological structure.* The recharge zones are mostly or partially known, whereas discharge zones are only partially known (Fig. 3.2,a) or unknown (Fig. 3.2,b).
4. *Closed hydrogeological structure.* The ground water system (aquifer) is completely isolated by impermeable geologic units and does not receive recharge. In fact, such a system can be discovered by drilling. The absence of any significant recharge either from the ground surface or adjacent aquifers is proved by continuing decrease in ground water head during pumping.

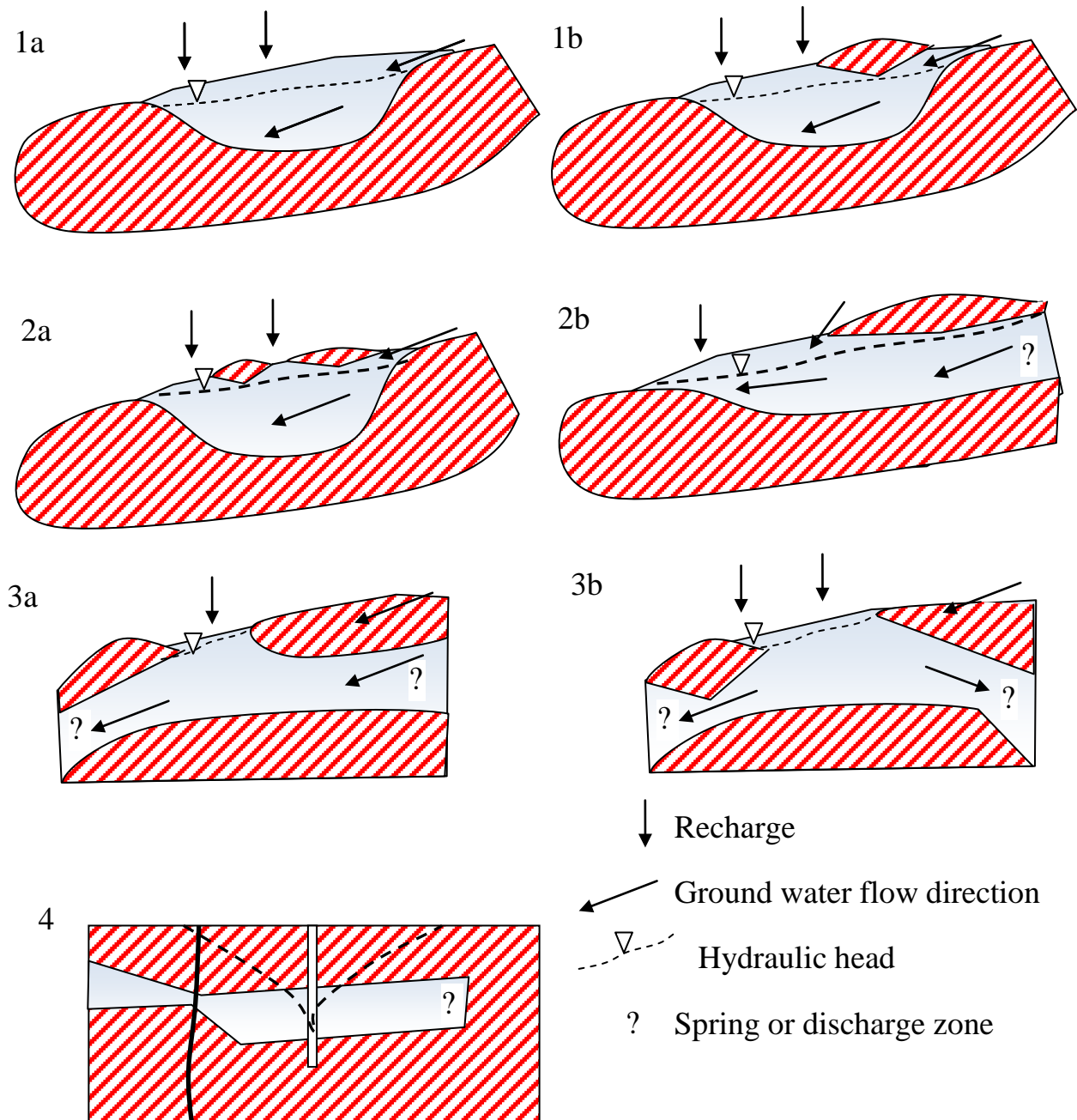


Fig. 3.2. Types of hydrogeological structures:
1 – open, 2 – semi-open, 3 – semi-closed, 4 – closed [36]

Key elements and geometry of ground water systems are illustrated in Fig. 3.3. Ground water system receives water via percolation, surface runoff, and surface water bodies through the *recharge area* on the land surface. As a part of the ground water system an aquifer may receive water from adjacent aquifers or dividing aquitards, however this kind of water income is not classified as recharge area. Sometimes the contacts between these aquifers refer to lateral or vertical recharge (discharge) areas.

Discharge area is defined as the area where the ground water system loses water (streams, lakes, wetlands, rivers, oceans). In an unconfined aquifer with the water table close to the soil surface water is lost as a result of evapotranspiration.

Drainage or contributing area gathers surface water runoff. *Ground water system extent* encompasses its limits. Ground water system geometry is always three-dimensional, so the two-dimensional cross-section can be insufficient to imagine and visualize some features of ground water flow.

The system contributing area, the extent, and the recharge area are usually not equal and can have different shapes depending on geology. For example, large regional confined aquifers may have smaller recharge areas compared to the aquifer extent, they may receive some portion of recharge through overlying aquitard or unconfined aquifer.

Defining the geometry of the aquifer system plays the key role in the majority of hydrogeological studies and has to determine

- (1) the contributing area or where the water origin is located;
- (2) the recharge area or where water is entering the system;
- (3) the aquifer extent or the ground water flow domain;
- (4) discharge area or where water is leaving the system.

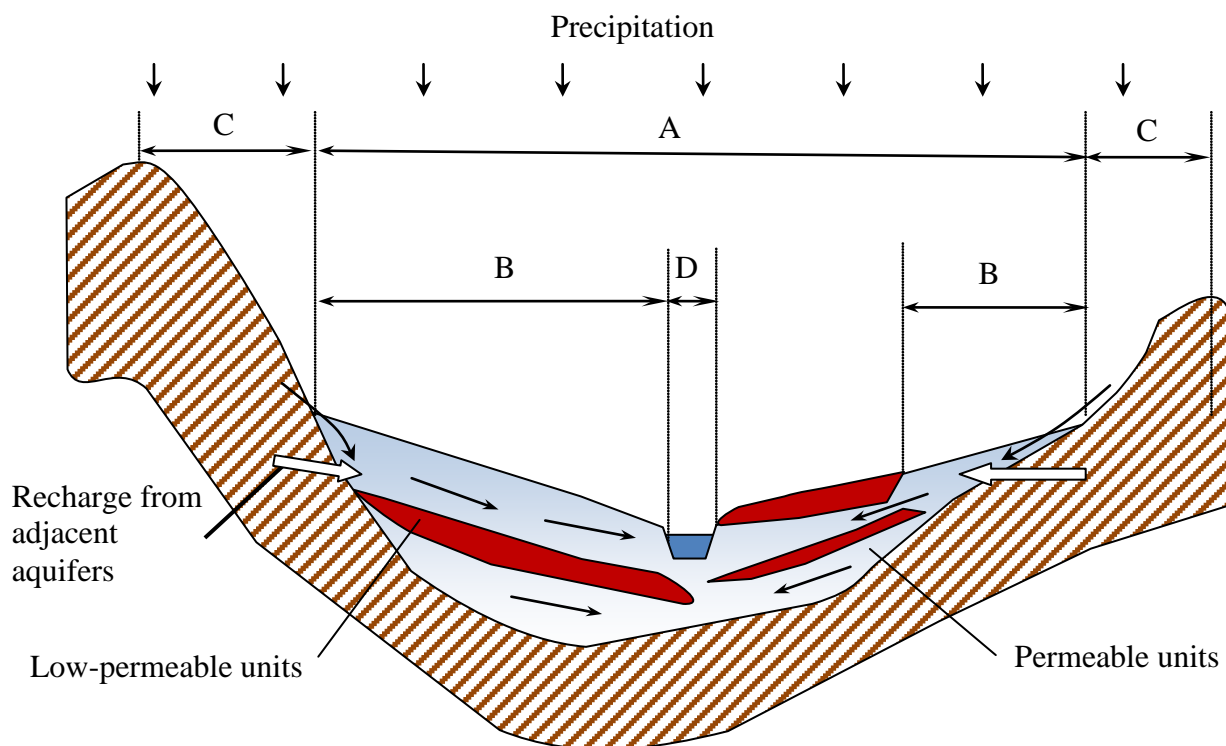


Fig. 3.3. Key elements of a ground water system. A – extent, B – recharge area, C – contributing (drainage area), D – discharge area [36].

3.2. Aquifer types

Sand and gravel aquifers. Sandstone aquifers. Carbonate (karst) aquifers. Basaltic and other volcanic rock aquifers. Fractured rock aquifers.

The most common classification of aquifers is based on lithology of the porous media. Regional characterization of aquifers for all continents is given in [37]. There are three main groups of aquifers, they are:

- 1) unconsolidated sediments,
- 2) sedimentary rocks,
- 3) fractured rock (bedrock) aquifers.

Low-permeable rocks and deposits cannot be considered as aquifers; they consist of unfractured igneous rocks, metamorphic rocks, shale, siltstone, evaporate deposits, silt, and clay.

Unconfined sand and gravel aquifers can be grouped into four categories [37]:

- 1) stream-valley aquifers, located beneath channels, floodplains, and terraces in the valleys of major streams;
- 2) basin-fill aquifers commonly occupying topographic valleys;
- 3) blanket sand and gravel aquifers;
- 4) glacial-deposit aquifers.

All these aquifers are characterized by inter-granular porosity and have inter-beds and layers of finer sediments (silt and clay) varying in thickness. They are the most productive and utilized aquifers worldwide because of (1) the highest total and effective porosity, (2) receiving more recharge owing to close location to the land surface, and (3) often direct hydraulic connection with surface water bodies serving as additional sources of recharge. For these reasons, some of the world's largest water well intakes are located in floodplains of main rivers. These water withdrawals involve additional recharge of surface waters filtering through aquifers from river banks.

Basin-fill aquifers consist of sand and gravel deposits partly filling depressions formed by faulting or erosion. Fine-grained deposits of silt and clay form confining beds retarding ground water flow. Deposits of considerable thickness become increasingly more compacted and low-permeable in depth. The basins are generally bounded by low-permeable igneous, metamorphic, and sedimentary rocks.

Basin-fill aquifers consist mostly of alluvial deposits eroded by streams from the rocks in upper parts of the basins. The sediments may locally include windblown sand, coarse-grained glacial outwash, and fluvial sediments. Coarser sediment including boulders, gravel, and sand is deposited near the basin borders, and finer sediment (silt and clay) is deposited in central part of the basins. Some basins contain lakes, watered or dried, near the centers. Sand and gravel of fluvial origin are located commonly in or adjacent to the channels of through-flowing streams. Basins in arid regions may contain deposits of salts, anhydrite, gypsum, or borate formed as a result of evaporation of mineralized water [41].

Basin-fill aquifers are recharged by infiltration of precipitation water that falls on the mountainous areas surrounding the basins. This recharge is intermittent

because of the intermittent nature of its source in mountains. As the streams go beyond the bedrock channels and flow in the alluvial valleys, the streamflow infiltrates the permeable deposits on the fans and moves downwards to the water table. In arid climate basins much water is lost by evaporation or transpiration.

Open basins are commonly connected hydraulically to adjacent basins. Some portions of recharge may enter an open basin as surface flow or ground water flow in the same direction as streamflow from upstream basins. Water discharges from basin-fill aquifers by evapotranspiration, as surface or subsurface flow into downstream basins. In case of intensive exploitation of aquifers or mining drainage most discharge is withdrawn from wells or shafts, which significantly changes water circulation. For example, mine drainage in the coal-mining basin Donbas has led to large depression on the area of thousands of square kilometers [79]; many wells in the western USA that were artesian before pumping dramatically decreased their yield [34].

Due to depletion the current ground water extraction is coming to deeper and more protected basin parts and aquifers that often still contain fossil or meteoric water. Intensive pumping from near-surface aquifers may lead in some cases to vertical upward migration of mineralized ground water. The second negative after-effect of ground water extraction from basin-fill aquifers is aquifer mining and decrease in storage, especially under poor natural recharge in arid regions.

Blanket sand and gravel aquifers consist largely of alluvial deposits brought in from mountain areas and deposited in lowlands. These aquifers are consolidated or semi-consolidated; they may contain windblown sand inside continents or beach or shallow marine sands in coastal zones [41].

Semi-consolidated sand aquifers consist of semi-consolidated sand, silt, and clay, confined by some carbonate rocks. The aquifers are water-laid and were deposited during a series of transgressions and regressions of the sea. Complex interbedding and lithology variations are the result of constantly changing conditions of deposition. Some hydrogeological units are thick and extended for tens to hundreds of kilometers, the others are only traceable [37]. Coastal plains aquifers are of great importance for water supply of population and industries in coastal zones; however, due to overexploitation in many locations the risk of seawater intrusion to ground water continues to increase with intensive pumping.

Glacial-deposit aquifers consist of sequences of glacial materials deposited either in former river valleys into bedrock or on the hills between the valleys. The glacial ice and melted water derived from the ice laid down several types of deposits collectively called “glacial drift”. *Till* deposited directly by ice consists of unsorted and non-stratified material of the size ranging from boulders to clay particles.

The distribution of numerous sand and gravel beds and interbedding in glacial-deposit aquifers is highly complex. The multiple advances and melting of continental ice have formed very heterogeneous deposit thickness including geological material of extremely varying grain size. The glacial-deposit aquifers are either localized in bedrock valleys or located in sheet-like deposits on outwash plains [41].

Sandstone aquifers are generally less permeable than sand and gravel aquifers; besides, their natural recharge is lower than surficial unconsolidated sand or gravel

aquifers. Nevertheless, sandstone aquifers are actually one of the important sources of water supply worldwide (Fig. 3.4).

Storage capacity of thick sandstone aquifers may be very significant; besides, owing to fracture porosity hydraulic conductivity of sandstones may be very high. Therefore, sandstone aquifers are very productive and provide large volumes of water for all users. Examples of continental-scale sandstone aquifers include the Guarani Aquifer System in South America, the Nubian Sandstone Aquifer System in Africa, and the Great Artesian Basin in Australia.

The Guarani Aquifer System includes the areas of Brazil, Uruguay, Paraguay, and Argentina; it extends on the area of 1,2 million km². Its volume is about 40000 km³, and water storage is sufficient to supply a population of 5,5 billion people for 200 years at a rate of 100 L/day [53]. The specific capacities of wells may reach 30 m³/hour/meter of drawdown with total dissolved solids (TDS) contents generally less than 200 mg/L. The production costs of water from wells are much lower than the costs of storing and treatment of surface water.

The Nubian Sandstone Aquifer System occupies the areas in Egypt, Libya, Sudan, and Chad. The thickness of permeable rocks varies from zero in outcrop areas to 3000 m in the central part. In some locations, confined aquifers provide water to high-yielding artesian wells. The quality of ground water in the Nubian basin is commonly high, TDS ranges from 0,1 to 1 g/L and increases towards the Mediterranean sea. In some shallow aquifers TDS reach 4 g/L. During the exploitation of the system over 40 billion m³ of water have been extracted, which resulted in drawdown that reaches 60 m in some areas. The estimated total recoverable volume of freshwater that is still available and can be extracted by four countries is about 14,5 thousand km³ [3].

The Great Artesian Basin in Australia is exploited since 1878. The total discharge of artesian wells reached the maximum in 1918 of almost 800 million m³ per year; currently due to the growing number of artesian boreholes it decreased more than twice. The accumulated discharge of these wells is about 1200 million L/d. High initial flow rates and pressures of artesian wells have diminished as a result of the release of elastic storage in the ground water reservoir; springs in some areas have ceased to flow [24].

Carbonate (karst) aquifers can be adequately characterized taking into account dual and even triple rock porosity that consists of matrix porosity, fracture porosity, and openings (karst conduits) formed as a result of leaching and solving rocks. Ground water in karst rocks can flow in fuzzy paths created by fractures and karst openings, which complicates evaluating aquifer properties and water well design.

In regional scale karst aquifers are characterized by the following features.

1. Ground water divides often do not coincide with surface water topographic divides as a result of loosening, sinking and drying streams.
2. Actual ground water velocities in some locations of aquifers may be extremely high, reaching hundreds of meters per day.
3. Aquifer discharge is often localized through large karst springs, which have subsurface drainage areas much larger than the topographic units.

The classical example is Dinaric karst in the Balkans, Europe; even the word “karst” comes from this area. The sequence of carbonate sediments is thousands of meters thick and deep borings encountered paleo-forms of karst more than 2000 m below the ground surface.

In ancient times karst aquifers in Europe and Asia were known to be used by streams in small and large facilities. Karst aquifers consist primarily of limestone and dolomite soluble by some mineralized waters. The largest concentration of fresh water springs in the world is in Florida (the USA) where there are about 700 springs of which 33 have the average discharge greater than 2,83 m³/s [37].

Extensive karst-originated subsidence of the ground surface appears near salt lakes and mines where salt has been extracted, for example at the village of Solotvino in Ukraine (Fig. 3.5). In the last decades these occurrences intensified (a sinkhole of 3000 m³ in 2010) and are threatening to infrastructures, primarily, the buildings in residential areas.

The karst in southwest China is known to be of fuzzy developed subsurface and surface topography. Carbonate rocks occupy one third of the total area 500 000 km², with dominating hills and mountains as landscape forms. Karst features were developed due to high infiltration rate, generally from 30 to 70% of precipitation. Karst aquifers store 40 to 70% of total ground water reserves in southwest China; there are 1293 documented significant springs that have the yield greater than 50 L/s [37].

Watered young coastal carbonate sediments of considerable thickness can be regarded as a significant source for local and centralized water supply, for example, in Caribbean, the Yucatan peninsula in Mexico, Philippines, and Sri Lanka [45].

Surface water can quickly enter karstified aquifers through a network of large fractures and dissolved openings that extend through the entire vadose zone. Therefore, any contaminant in the infiltrating water from the surface can reach the water table and migrate faster than in porous aquifers. For this reason karst aquifers are more vulnerable to contamination and have to be protected more strictly than other aquifers.

Extensive lava flows occur in west-central India, where the Deccan basalts occupy an area larger than 500 000 km². Other volcanic terrains are located in Central America, Central Africa, in islands of volcanic origin (Hawaii, Iceland, and the Canaries). Some of the massive lavas are almost impermeable as the Deccan; in contrast, the thin fractured lavas are good conduits of water but they have small storage. Leakage from overlying thick, porous, but low-permeable volcanic ash may act as the storage for the two-layer system, for example, in the aquifer system located in Central America (Salvador, Nicaragua, and Costa-Rica).

Fractured rock aquifers are developed in igneous and metamorphic rocks. These rocks are commonly low-permeable, however, when fractured they may yield significant volumes of water. In many mountainous places of the globe fractured rock aquifers are the only reliable source of water supply. These aquifers are usually associated with specific types of rocks. The upper part of the fractured rock aquifers is more weathered and contain residual of clays, below the rock it becomes more consolidated being transformed into the fractured bedrock.



Fig. 3.4. Hoodoo Sandstone Structures, Bryce Canyon, National Park, Utah, USA [28]



Fig. 3.5. Karst occurrences in Solotvino (Ukraine) [31]

Section review

1. Define the aquifer as a hydrogeological unit.
2. Describe the difference between confined and unconfined aquifers.
3. Can the same aquifer be confined and unconfined in different areas? Under which conditions?
4. Describe the difference between the terms “aquitard” and “aquiclude”. Which term is more general?
5. Compare semi-open and semi-closed hydrogeological structures in terms of water circulation.
6. In which case water inflow enters the aquifer not from the recharge areas?
7. What are the main issues of hydrogeological studies?
8. Describe the main elements of a ground water system.
9. Characterize the features of sand and gravel aquifers.
10. Describe the specifics of basin-fill aquifers.
11. Describe the specifics of semi-consolidated aquifers.
12. Compare the heterogeneity of basin-fill, semi-consolidated, and glacial deposit aquifers.
13. Compare the significance of sand/gravel and sandstone aquifers for ground water industry.
14. Compare the storage capacity of sand/gravel and sandstone aquifers.
15. Give the examples of the well known and large aquifer systems.
16. Describe the main difficulties in exploitation of carbonate (karst) aquifers.
17. Describe the major features of basaltic and fractured rock aquifers.
18. Describe the major features of aquifers.

4. HYDRAULIC PROPERTIES OF SOILS AND ROCKS

4.1. Storage properties

Porosity. Storage and storativity. Specific storage. Specific yield. Ground water mining and land subsidence.

Porosity. *Total porosity* of soil or rock is defined as the ratio of the volume of voids to the total volume of material

$$n_t = \frac{V_v}{V_t} = \frac{V_t - V_s}{V_t}, \quad (4.1)$$

where n_t is total porosity, V_v is the volume of voids, V_s is the volume of solid phase, V_t is the total volume. Sometimes porosity is expressed in per cents.

Primary porosity includes the original voids (interstices) formed during the creation of soil or rock. These voids comprise pores in soil or sedimentary rocks, as well as lava tubes and fractures in basalt (Fig. 4.1). *Secondary porosity* refers to joints, faults in igneous, metamorphic and consolidated sedimentary rocks, and openings in carbonate and other soluble rocks. Primary and secondary porosities can be successively altered many times, which completely changes the original nature of the rock porosity. This may result in porosity variations without significant change of the overall void volume.

Porosity can be also defined in terms of density

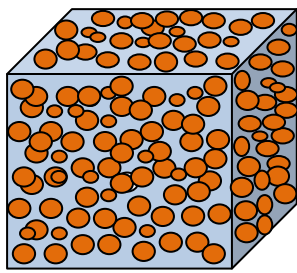
$$n_t = 1 - \frac{\rho_b}{\rho_s}, \quad (4.2)$$

where ρ_b is the bulk density (related to dry soil or rock sample), ρ_s is the density of solids.

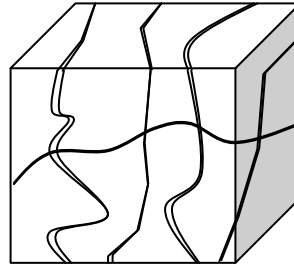
The porosity of soil or rock depends on the degree of grain compaction (Fig. 4.2), the grain shape, and the particle size distribution. For the material of spheres of equal size the compaction reduces the porosity, the minimum of porosity will be at the angle θ between sphere centers equal to 90° (Fig. 4.2,c), the maximum porosity is reached at the angle θ equal to 60° (Fig. 4.2,a).

The multiple shapes of the grains can cause deviations from the average porosity value, depending on arrangement and connection of grains. A geological material containing sorted grains possesses usually higher porosity than poorly sorted material because small-size particles occupy the voids between large grains.

The porosity of natural soils or rocks varies from zero to 60% (Table 4.1). As a rule, the porosity of unlithified materials is much higher than for the lithified materials significantly transformed in course of geological development. For unlithified sediments, the smaller the size of grains, the higher the porosity.

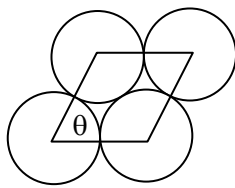


a)

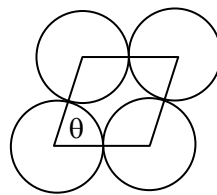


b)

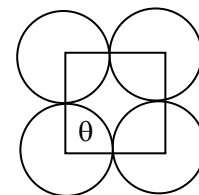
Fig. 4.1. Pore space geometry in sedimentary soils (a) and fractured rocks (b)



a)



b)



c)

Fig. 4.2. Compaction patterns of grains as equal size spheres [62].

Table 4.1

Range of porosity values (in fractions of 1,0) [6, 46, 59]

Material	Total porosity	Effective porosity
Gravel	0,24 – 0,38	0,13 – 0,40
Sand	0,26 – 0,53	0,01 – 0,46
Silt	0,34 – 0,51	0,01 – 0,39
Clay	0,34 – 0,57	0,01 – 0,18
Sandstone	0,14 – 0,49	0,12 – 0,41
Siltstone	0,21 – 0,41	0,01 – 0,33
Limestone	0,07 – 0,56	0,00 – 0,36
Basalt	0,03 – 0,35	N/A
Weathered granite	0,34 – 0,57	N/A
Weathered gabbro	0,42 – 0,45	N/A

N/A = not available

Usually, not all of the voids are involved in water flow, both in fractured and sedimentary rocks. Although the unfractured shale contains water-filled pores, almost all of the flow takes place through the fractures providing the effective pathways for flow through interstices in rock. *Effective porosity* is defined as the volume of interconnected pores that allow free gravity water to flow. Effective porosity is more

important for ground water flow than total porosity. Thus, the dual porosity concept applicable mostly to fractured rocks distinguishes the effective porosity in high-permeable fractures occupying insignificant volume and the total porosity that additionally includes the voids in low-permeable porous blocks.

Storage and storativity. Hydrogeological units have the ability to store water. Ground water release from storage in unconfined and confined aquifers can be quantified by the parameters of specific yield and coefficient of storage. When a well is pumped in a confined aquifer, the declining hydraulic head in the vicinity of the well enables the pressurized water to expand slightly, adding a small volume of water. This lets the aquifer collapse gradually, compensating water withdrawal. The main source of water in an unconfined aquifer is the drainage from pores as the response to pumping. An unconfined aquifer releases much more water from storage than a confined aquifer.

The *storativity* S of an aquifer is defined as the volume of water that an aquifer releases from or takes into storage per unit surface area of the aquifer per unit change in head.

$$S = \frac{\text{volume of water}}{(\text{unit area})(\text{unit head change})} = \frac{\text{m}^3}{\text{m}^3}. \quad (4.3)$$

In a confined aquifer, storativity values range from 10^{-3} to 10^{-5} .

Specific storage quantifies how much water is stored in aquifer. *Specific storage* S_s is defined as the volume of water that an aquifer releases from or takes into storage per unit surface area of the aquifer per unit aquifer thickness per unit change in head.

$$S_s = \frac{\text{volume of water}}{(\text{unit area})(\text{unit head change})} = \frac{1}{\text{m}}. \quad (4.4)$$

Specific storage is related to storativity by

$$S = S_s b, \quad (4.5)$$

where b is the aquifer thickness.

The specific storage in a confined aquifer is defined as

$$S_s = \rho_w g (\beta_p + n\beta_w), \quad (4.6)$$

where ρ_w is the water density, $g = 9,81 \text{ m/s}^2$, n is the porosity of the aquifer, β_p is the vertical compressibility of rock matrix, and β_w is the compressibility of water. The compressibility of ground water $\beta_w = 4,8 \cdot 10^{-10} \text{ m}^2/\text{N}$ at 25°C . Eq. 4.6 can be used to evaluate specific storage and storativity of some aquifers.

The ground water response to pumping in an unconfined aquifer is different from that in a confined aquifer. Near the beginning, when there is no significant change of the water level, water comes from its expansion and compression of grains. Then, water comes largely from the gravity drainage of pores in the aquifer. The storativity of an unconfined aquifer is expressed as

$$S = S_y + b S, \quad (4.7)$$

where S_y is the specific yield of the aquifer.

The difference in water volume released after sinking ground water table and piezometric surface is shown in Fig. 4.3 taking into account [26].

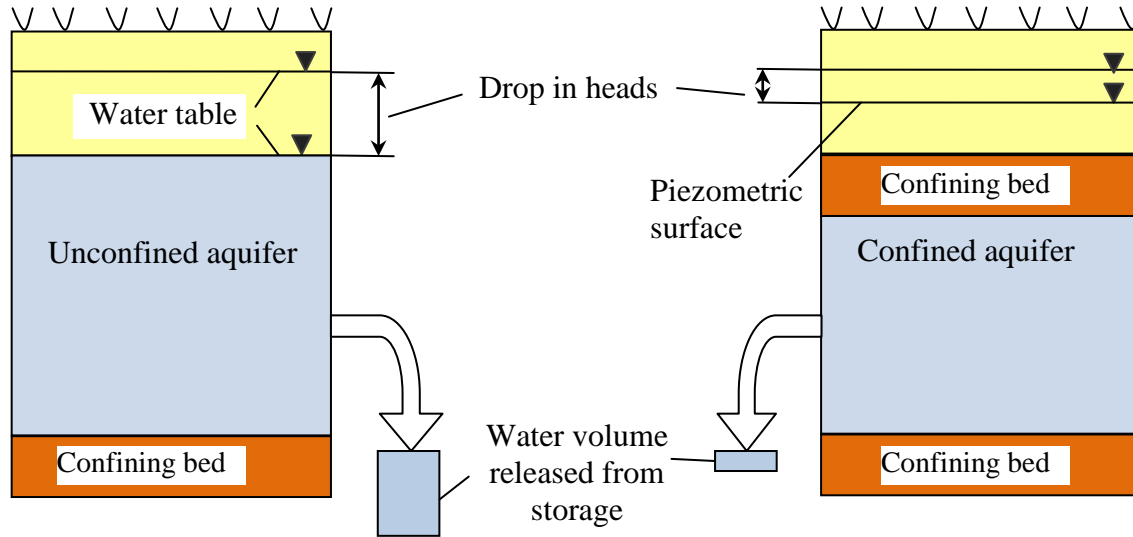


Fig. 4.3. Storativity in confined and unconfined aquifers

Example. A confined aquifer is composed of dense sand with a thickness of 100 m and a porosity of 25%. The compressibility of dense sand varies from $6,25 \cdot 10^{-7}$ to $1 \cdot 10^{-6} \text{ m}^2/\text{N}$. Estimate the range for specific storage and storativity. A total head drop in the area of 1000 km² was 100 m. How much water is released from the storage?

Solution. The specific storage caused by compressibility of water is

$$S_{s,w} = \rho_w g n \beta_w = 1000 \frac{\text{kg}}{\text{m}^3} \cdot 9,81 \frac{\text{m}}{\text{s}^2} \cdot 0,25 \cdot 4,8 \cdot 10^{-10} \frac{\text{m}^2}{\text{kg} \cdot \text{m}/\text{s}^2} = 1,18 \cdot 10^{-6} \frac{1}{\text{m}}.$$

The specific storage caused by compressibility of soil solid particles is

$$S_{s,m} = \rho_w g \beta_p = 1000 \frac{\text{kg}}{\text{m}^3} \cdot 9,81 \frac{\text{m}}{\text{s}^2} \cdot (1,3 \div 2,0) \cdot 10^{-8} \frac{\text{m}^2}{\text{kg} \cdot \text{m}/\text{s}^2} = (1,27 \div 1,96) \cdot 10^{-4} \frac{1}{\text{m}}.$$

The specific storage for the aquifer is

$$S_s = S_{s,w} + S_{s,p} = 1,18 \cdot 10^{-6} \frac{1}{\text{m}} + (1,27 \div 1,96) \cdot 10^{-4} \frac{1}{\text{m}} = (1,28 \div 1,97) \cdot 10^{-4} \frac{1}{\text{m}}.$$

The storativity due to the compressibility of water is

$$S^W = S_{s,w} b = (100\text{m}) \cdot 1,18 \cdot 10^{-6} \frac{1}{\text{m}} = 1,18 \cdot 10^{-4}.$$

The storativity due to the compressibility of solid matrix is

$$S^M = S_{s,s} b = (100\text{m}) \cdot (1,28 \div 1,97) \cdot 10^{-4} \frac{1}{\text{m}} = (1,28 \div 1,97) \cdot 10^{-2}.$$

The overall storativity due to the compressibility of water is

$$S = S^W + S^M = 1,18 \cdot 10^{-4} + (1,28 \div 1,97) \cdot 10^{-2} = (1,29 \div 1,98) \cdot 10^{-2}.$$

The volume of water that can be withdrawn from the storage due to sinking hydraulic head of 100 m in the area of 1000 km² is

$$V = S \Delta h A = (1,29 \div 1,98) \cdot 10^{-2} \frac{1}{m} \cdot 100m \cdot 10^9 m^2 = (1,29 \div 1,98) \cdot 10^9 m^3.$$

In this example, most of the water comes from compression of the matrix. In some areas this could lead to land subsidence.

Specific yield. This parameter ranges from 0,1 to 0,3, while the product of aquifer thickness and specific storage is estimated in the range from 10⁻³ to 10⁻⁵. Therefore, specific yield is the major part of storage in an unconfined aquifer.

In some areas an aquifer can be confined in some areas and unconfined in others, for example, due to pumping and developing in time the cone of depression. In case of aquifer transition from confined to unconfined storativity values change accordingly.

The *specific yield* of soil or rock is defined as the volume of water in the pore space that can be freely drained due to sinking of the water table. The volume of water retained by a porous material, which cannot be easily drained by gravity, is called *specific retention*. Together, specific yield and specific retention are equal to the total porosity of soil or rock. The specific retention increases when grain size or pore size of soils or rocks decrease (Table 4.2).

Table 4.2

The values of porosity, specific yield, and specific retention (in fractions of 1,0) [27]

Material	Porosity	Specific yield	Specific retention
Soil	0,55	0,4	0,15
Clay	0,50	0,02	0,48
Sand	0,25	0,22	0,03
Gravel	0,20	0,19	0,01
Limestone	0,20	0,18	0,02
Sandstone (semi-consolidated)	0,11	0,06	0,05
Granite	0,10	0,09	0,01
Basalt (young)	0,11	0,08	0,03

Ground water mining and land subsidence. Ground water is usually withdrawn from the storage in soils and rocks, regardless of the recharge conditions. This means that water has to be stored in subsurface voids before extraction.

The portion of the saturated zone that changes its thickness in response to natural recharge represents dynamic storage (Fig. 4.4). For unconfined aquifers the dynamic storage is limited by variations of ground water level and vary widely

depending on seasonal and long-term fluctuations of recharge including precipitation. In the absence of anthropogenic ground water withdrawal this storage can be considered as completely renewable.

The domain of the saturated zone below the mean annual water level has constant volume of stored ground water and is called static storage. In the presence of anthropogenic ground water withdrawal, the static storage can decrease in case the volume of extracted water exceeds the dynamic storage. Such process is called aquifer mining and results in continuous decline of hydraulic heads and spring flows.

The static storage does not change if the withdrawal equals dynamic storage. On the contrary, the renewable dynamic storage can increase in case of natural recharge due to ground water pumping. This phenomenon occurs for ground water intake near surface water bodies (Fig. 4.5). In this case the ground water system does not discharge into surface waters. The reliable assessment of storage components is possible only in the presence of the long-term monitoring data on changing hydraulic head, as well as water balance constituents.

The static storage capacity may be significantly changed by extensive ground water withdrawal. As a result of declining hydraulic head the water pressure supporting the overlying material drops, which leads to shifting sediment pore space to the granular skeleton and decreasing porosity (Fig. 4.6). Sand and gravel deposits are relatively incompressible, therefore the volume of the aquifers does not change significantly. In contrast, clay and silt confining beds can be compressed as a result of squeezing water. Total weight of the overlying rocks and water above the aquitard (Fig. 4.6,a) is balanced by the fluid pore pressure and effective stress in solid phase. Ground water withdrawal reduces fluid pore pressure, which increases effective stress and leads to irreversible aquifer compaction and land subsidence (Fig. 4.6,b).

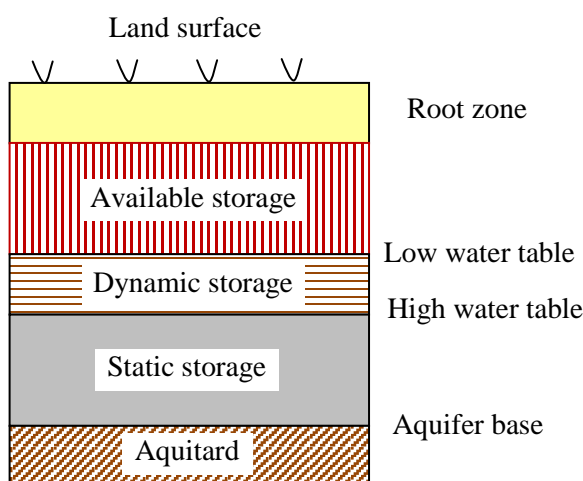


Fig. 4.4. Ground water storage components in an unconfined aquifer

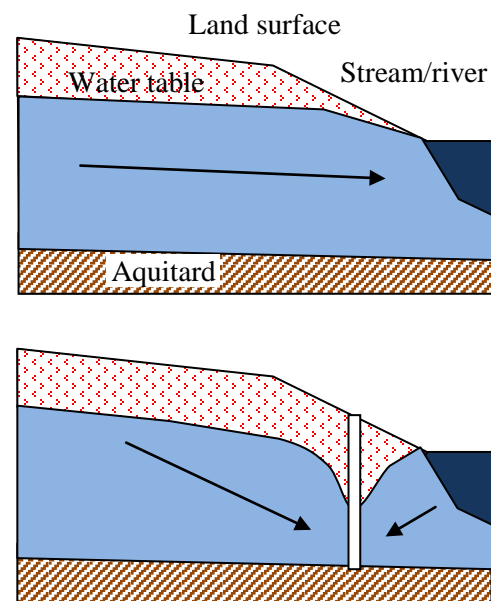


Fig. 4.5. Induced aquifer recharge due to ground water withdrawal near a surface water body

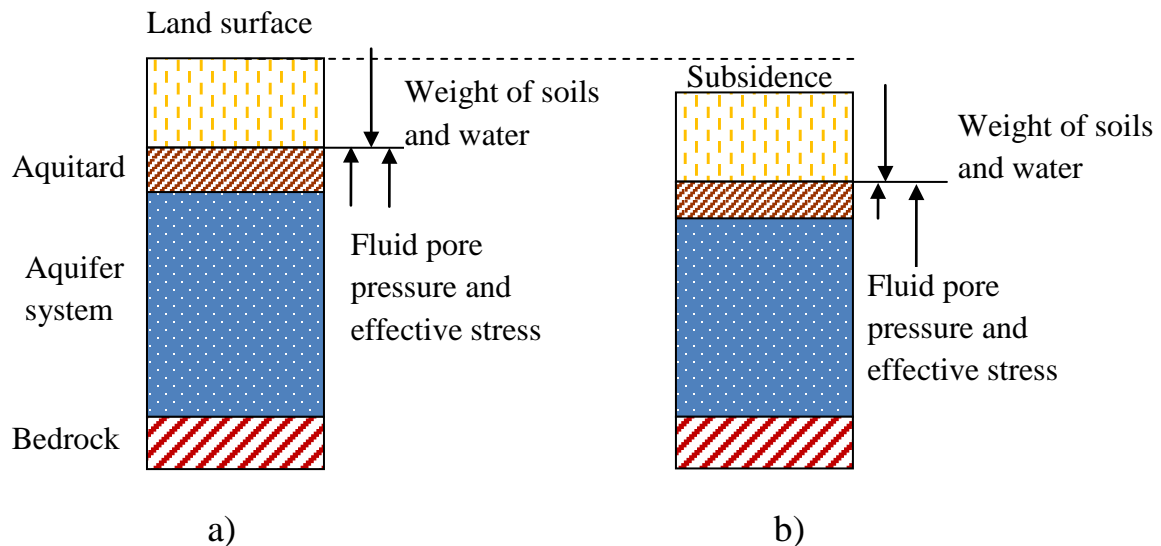


Fig. 4.6. Scheme of ground subsidence caused by water withdrawal from aquifer:
a) before pumping, b) after pumping.

Soil and rock compaction depends on thickness and hydraulic conductivity, type and structure. Clays and silts have higher elasticity in comparison to sands and gravels. Thus, clay and silt compaction can continue for months and years after the water level becomes stable in the aquifer. The confined aquifer systems containing significant clay and silt layers are vulnerable to intensive large-scale ground water withdrawals. The volume of water coming from irreversible compaction usually ranges from 10 to 30% of the total volume of water pumped. This leads to a permanent reduction in the storage capacity of the aquifer system.

There were a number of examples demonstrating land subsidence caused by aquifer mining. The well known cases in North America are Santa Clara Valley (“Silicon Valley”) in California, Mexico City, and Las Vegas Valley. The most significant subsidence (9 m) has been documented in San Joaquin Valley in California as a result of intensive ground water withdrawal for irrigation purposes.

Example. The weight of the sample drained by gravity is 100 g. After the sample is oven-dried its weight lowers to 92 g. The bulk density of the soil is $1,7 \text{ g/cm}^3$. Calculate the specific yield, specific retention, and porosity of the sample assuming the water mass drained by gravity is 23 g.

The total volume sample is

$$V_t = \frac{100 \text{ g} + 23 \text{ g}}{1,7 \text{ g/cm}^3} = 72,35 \text{ cm}^3.$$

The volume of water (its density $1,0 \text{ g/cm}^3$) retained after draining is

$$V_r = \frac{100 \text{ g} - 92 \text{ g}}{1,0 \text{ g/cm}^3} = 8 \text{ cm}^3.$$

Similarly, the volume of water drained by gravity is $V_d = 23 \text{ cm}^3$.

The specific retention is

$$S_r = \frac{V_r}{V_t} = \frac{8 \text{ g/cm}^3}{72,35 \text{ g/cm}^3} = 0,11 .$$

Specific yield is

$$S_y = \frac{V_d}{V_t} = \frac{23 \text{ g/cm}^3}{72,35 \text{ g/cm}^3} = 0,32 \text{ or } 32\% .$$

Therefore, porosity of the sample is calculated as follows

$$n = S_r + S_y = 0,11 + 0,32 = 0,43 \text{ or } 43\% .$$

4.2. Hydraulic conductivity

Hydraulic head. Hydraulic gradient. Hydraulic conductivity. Intrinsic permeability. Grain size distribution. Transmissivity.

Hydraulic head. The total energy or the impelling force for water flow at an arbitrary point of the aquifer is defined as

$$H = z + h_p + \frac{v^2}{2g}, \quad (4.8)$$

where z is the elevation above datum (datum usually means sea level, it can also be any reference level); h_p is the pressure head due to the ground water pressure above that point; v is the velocity of water flowing through pores, g is the acceleration of gravity (Fig. 4.7).

In most cases ground water flow velocity is very low; therefore, the velocity head (the third factor of the Eq. 4.8) can be neglected for practical purposes and this equation becomes

$$H = h = z + h_p, \quad (4.9)$$

where h is the *hydraulic head*, called also *piezometric level*. The pressure head represents the pressure of fluid p of constant density ρ at that point of aquifer.

$$h_p = \frac{p}{\rho g}. \quad (4.10)$$

The surface dividing saturated zone with pores completely filled with water solution where fluid pressure exceeds atmospheric pressure and unsaturated zone is called *ground water level* or *ground water table*.

In practice, the hydraulic head is determined in observation wells or piezometers by subtracting the measured depth to the water head from the surveyed elevation of the top of the casing.

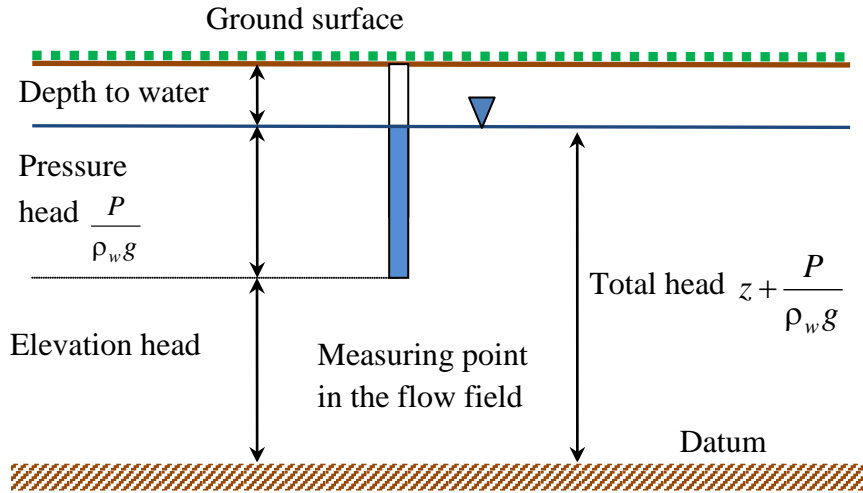


Fig. 4.7. Hydraulic head in ground water flow [8]

Flowing ground water loses its energy due to friction between its particles and the porous geological material. The loss of energy equals to a decrease in the hydraulic head measured at point “1” and point “2”.

$$\Delta h = h_1 - h_2. \quad (4.11)$$

Hydraulic gradient is defined as the change in hydraulic head in a given direction

$$i = -\frac{\Delta h}{\Delta l} = \frac{h_1 - h_2}{\Delta l}, \quad (4.12)$$

where h_1 and h_2 are the hydraulic heads at points “1” and “2”, respectively, and Δl is the distance between two points. The hydraulic gradient i in Eq. 4.12 is the gradient from the point “1” to the point “2”.

Ground water always flows from the higher hydraulic head towards the lower hydraulic head. Sometimes, however, a small portion of water can flow upward from the aquifer but this case is not a strictly horizontal flow (Fig. 4.8). In the area of the aquifer recharge the flow is vertically downward and laterally towards the discharge area; in contrast, in the discharge area like surface stream the flow has an upward component.

It is possible to install a number of piezometers to contour head values in the field. For each point of the ground water flow domain the head can increase in some directions and decrease in others. The gradient is oriented to the direction of the maximum head decrease and perpendicular to the lines of equal hydraulic head called as equipotential lines.

At least three hydraulic gradient measurements are needed to calculate the hydraulic gradient and the direction of ground water flow. Below are the calculation steps. The results of measurements are shown on Fig. 4.9.

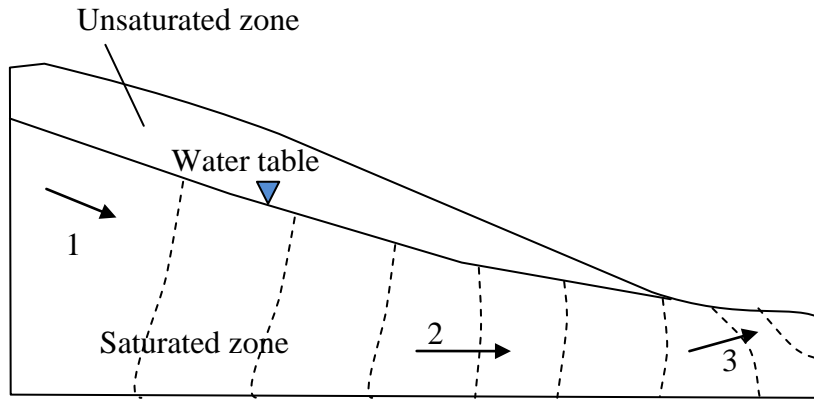


Fig. 4.8. Ground water flow in vertical section:

1 – downward, 2 – horizontal, 3 – upward.

Dashed lines are equipotentials, arrows show ground water flow direction

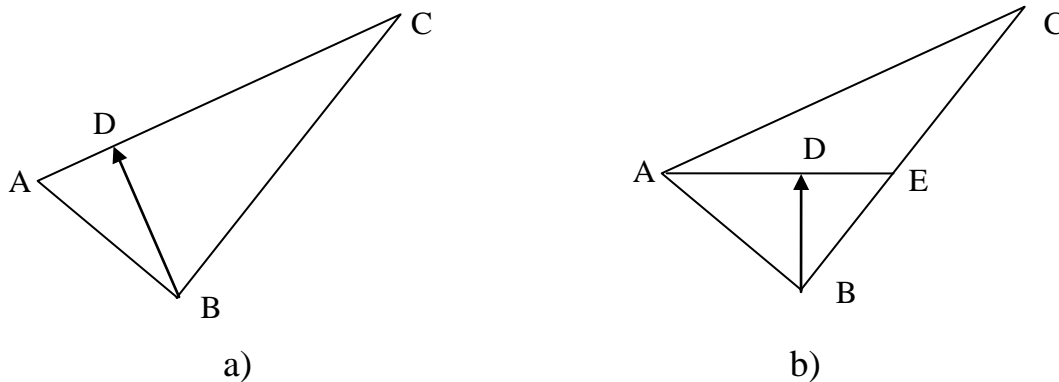


Fig. 4.9. Determination of flow direction (see explanations below)

Denote the heads at the wells A , B , and C as h_A , h_B , and h_C .

1. Make sure that the three hydraulic heads in three wells (A , B , and C) are not equal. If $h_A = h_B = h_C$, then no flow occurs.
2. If the hydraulic heads in two of the wells are equal (f. e. $h_A = h_B$) as shown in Fig. 4.9,a, draw a line through C and perpendicular to AB till the intercept point D . If $h_C > h_A$ and $h_C > h_D$, then ground water will flow from C to D and

$$i_{CD} = \frac{h_C - h_D}{CD}. \quad (4.13)$$

3. If the hydraulic heads are different at the three wells as shown in Fig. 4.9,b, it has to find a location E on the line connecting the well with the highest head (here C) to the well with the lowest head (here B), at which the head is the same as that in the intermediate well (A). Then draw a line between A and E and another line through C , intercepting the line AE . Ground water flow will be directed from C to D as shown by the arrow. Then the hydraulic gradient is calculated by Eq. 4.13.

Exercise. For the given heads at the wells A, B, and C find the flow direction and calculate the hydraulic gradient.

#	h_A , m	h_B , m	h_C , m
1	120	130	140
2	130	130	140
3	135	130	120

Hydraulic conductivity is the constant of proportionality relating the specific discharge to the hydraulic gradient. This parameter quantifies the ease with which a fluid flows through a geological material. It has relatively large values for permeable units like sand or gravel, and relatively small values for low-permeable materials like clay or shale.

The dimensionality of hydraulic conductivity is the same as velocity, m/s in the SI System or m/day. There are also other dimensions, primarily in the USA and UK, for example, gallons per day per foot squared used in English Engineering Unit System.

There are a number of thousands of hydraulic conductivity values established for various rocks and soils. Some of the values are brought together in Table 4.3.

Table 4.3

Ranges of hydraulic conductivity for various rock types [8]

Rock type	Material	Hydraulic conductivity, m/s
<i>Sedimentary</i>	Gravel	$3 \cdot 10^{-4} - 3 \cdot 10^{-2}$
	Coarse sand	$9 \cdot 10^{-7} - 6 \cdot 10^{-3}$
	Medium sand	$9 \cdot 10^{-7} - 5 \cdot 10^{-4}$
	Fine sand	$2 \cdot 10^{-7} - 2 \cdot 10^{-4}$
	Silt, loess	$1 \cdot 10^{-9} - 2 \cdot 10^{-5}$
	Clay	$1 \cdot 10^{-11} - 4,7 \cdot 10^{-9}$
<i>Sedimentary rocks</i>	Karst and reef limestone	$1 \cdot 10^{-6} - 2 \cdot 10^{-2}$
	Limestone, dolomite	$1 \cdot 10^{-9} - 6 \cdot 10^{-6}$
	Sandstone	$3 \cdot 10^{-10} - 6 \cdot 10^{-6}$
	Siltstone	$1 \cdot 10^{-11} - 1,4 \cdot 10^{-8}$
	Shale	$1 \cdot 10^{-13} - 2 \cdot 10^{-9}$
<i>Crystalline rocks</i>	Permeable basalt	$4 \cdot 10^{-7} - 2 \cdot 10^{-2}$
	Fractured igneous and metamorphic rocks	$8 \cdot 10^{-9} - 3 \cdot 10^{-4}$
	Weathered granite	$3,3 \cdot 10^{-6} - 5,2 \cdot 10^{-5}$
	Basalt	$2 \cdot 10^{-11} - 4,2 \cdot 10^{-7}$
	Unfractured igneous and metamorphic rocks	$3 \cdot 10^{-14} - 2 \cdot 10^{-10}$

Intrinsic permeability. Experiments have shown that hydraulic conductivity depends not only on properties of geological material but also on fluid properties (density and viscosity). Explicitly this can be demonstrated by the relationship between hydraulic conductivity and intrinsic permeability (or permeability).

$$K = \frac{\kappa \rho_w g}{\mu}, \quad (4.14)$$

where κ is the intrinsic permeability, ρ_w is the water density, $g = 9,81 \text{ m/sec}^2$, μ is the dynamic viscosity of water, $\text{kg}/(\text{m}\cdot\text{sec})$.

The intrinsic permeability of soil or rock is the measure of its ability to transmit fluid or gas through itself. The permeability does not depend on the properties of fluid or gas. Usually permeability is measured in m^2 , or cm^2 , or in darcy; below are the equations to convert units

$$1 \text{ m}^2 = 10^4 \text{ cm}^2 = 1.013 \cdot 10^{12} \text{ darcy}.$$

Viscosity and density are functions of pressure and temperature. At 20°C and pressure of 1 atm, the density and dynamic viscosity of water are $998,2 \text{ kg/m}^3$ and $1,002 \cdot 10^{-3} \text{ kg}/(\text{m}\cdot\text{sec})$. Under these conditions the hydraulic conductivity of soil or rock is calculated as

$$K = \left(9,77 \cdot 10^6 \frac{1}{\text{m} \cdot \text{sec}} \right) \kappa, \quad (4.15)$$

where K is in m/s and κ in m^2 . Intrinsic permeability can be converted from hydraulic permeability as follows

$$\kappa = (1,023 \cdot 10^{-7} \text{ m} \cdot \text{sec}) K. \quad (4.16)$$

Example. A crystalline rock has the permeability of 1 m/day or $1,16 \cdot 10^{-5} \text{ m/s}$. Define the likely rock or soil, which could have the indicated permeability and calculate its intrinsic permeability.

According to Table 4.2 this could be permeable basalt, fractured igneous and metamorphic rock or weathered granite. Applying Eq. 4.16 we determine the intrinsic permeability of this rock that equals $1,18 \cdot 10^{-12} \text{ m}^2$.

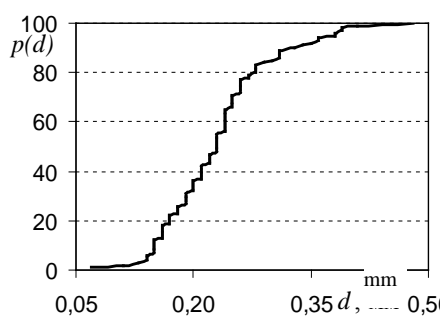
The intrinsic permeability of soil or rock is related to the grain diameter and porosity. A number of empirical equations have been derived to estimate the intrinsic permeability and hydraulic conductivity from grain-size properties (Table 4.4).

The *effective grain diameter* is the grain size of the smallest 10% of the grains. The grain size distribution (see examples on Fig. 4.10) is determined directly by sieve analysis. The particle distribution of fine-grained soils is indirectly determined by hydrometer analysis. A sieve analysis includes passing a sample through a set of sieves and weighting the amount of material retained in each sieve. Hydrometer analysis should be performed on only the fraction passing the sieve having the openings of 0,074 mm [59].

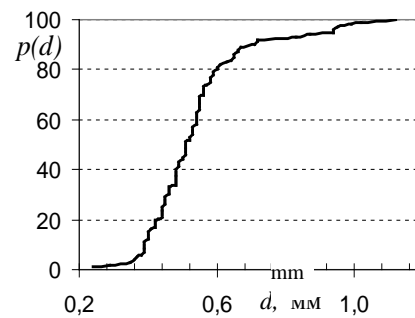
Table 4.4

Empirical formulae to calculate hydraulic conductivity [25, 59]

#	Author	Formula	Notations
1	A. Hazen	$K = cd_{10}^2(0.7 + 0.03T)$	c is the empirical factor ranging from 400 for clayey sand to 1200 for sand; T is temperature, °C. The formula is applicable, if $0.1 \text{ mm} < d_{10} < 3 \text{ mm}$.
2	Th. Krueger	$K_{10} = \frac{322n}{(1-n)^2} d_q^2,$ $d_q = \frac{100}{\sum_{i=1}^N g_i / d_i}$	N is the number of grain size fractions; d_i is grain size, mm; g_i is the content of i -th fraction in the soil, %; n is dimensionless porosity; d_q is active size; K_{10} is hydraulic conductivity at 10 °C. The formula is recommended to mid-grain sands.
3	F. Zunker	$K_0 = \frac{cn^2}{(1-n)^2} \frac{(1+0.034T)}{s^2},$ $s = \frac{3g_2}{2d_1} + \sum_{i=2}^N \frac{g_i \left(\frac{1}{d_{i-1}} - \frac{1}{d_i} \right)}{\ln d_i - \ln d_{i-1}}$	K_0 is hydraulic conductivity at 0 °C, s is specific surface; c is the empirical factor ranging from 340 for nonuniform sand to 1160 for uniform sand with well-rounded grains; g_2 is the weight content of individual fractions present in the soil; the rest notations are the same as above. The formula is more applicable to mid-grain sands and fine sands.



a)



b)

Fig. 4.10. Grain size distributions of two materials: a) mid-grain sand, b) coarse sand; $p(d)$ is the percentage of grains with the size less than d

Transmissivity quantifies the ease with which water can move through an aquifer [59]. This is the rate at which water of prevailing viscosity is transmitting

through a unit width of the aquifer under a unit hydraulic gradient. The transmissivity is calculated as

$$T = b K, \quad (4.17)$$

where K is the hydraulic conductivity of the aquifer, b is the aquifer thickness.

The transmissivity of a thin aquifer composed of permeable deposits can be greater than of thick aquifer containing low-permeable materials. For example, the transmissivity of a gravel aquifer (let $b = 15$ m and $K = 20$ m/d) equals to $300 \text{ m}^2/\text{day}$, which exceeds the transmissivity of basaltic rock aquifer (let $b = 50$ m and $K = 1,5$ m/d) that equals to $75 \text{ m}^2/\text{day}$. Therefore, the parameter T characterizes the aquifer in terms of its capability of yielding water for supply, in other words, it estimates the aquifer economically.

4.3. Heterogeneity and anisotropy

Representative elementary volume. Heterogeneity. Fractured rocks. Anisotropy.

Representative elementary volume. Hydraulic properties of soil and rock include the properties that govern the capacity to hold and transmit water (effective porosity, specific retention, hydraulic conductivity, and storativity). They refer to the so-called representative volume of a geological material in which they can be evaluated. The properties described below are assumed to be defined in the representative volume.

Soil and rock can be classified as homogeneous and heterogeneous depending on the volume selected to determine its properties. The relatively small zone of soil or rock in an aquifer is called the *representative elementary volume*, if the properties of the geological material and flow characteristics can be properly defined within this volume. This definition is rather theoretical because deciding what has to be the size of this volume needs thorough analysis of field data, interpolation and performing laboratory tests.

For example, one cubic decimeter can be a sufficient volume to evaluate, more or less credibly, the properties of sand or loamy sand. The same volume is evidently insufficient to evaluate permeability of rock with very rarely sparse fractures; for this case the representative volume of at least some cubic meters is recommended.

Another problem in evaluating parameters of soils and rocks is upscaling. This term means the process of applying the parameter values obtained in laboratory to a field scale area (aquifer). Commonly, due to heterogeneity the aquifer parameters, preliminary evaluated in laboratory, need to be corrected after field scale tests.

Heterogeneity. *Homogeneous* geological material has equal properties in any directions. Beach sand sorted can be an example of homogeneous unconsolidated soil. *Heterogeneous* soils or rocks have different properties in different parts of a material.

Most of soils are actually the mixtures of geological materials with different properties. For example, alluvial aquifers consist of sand, gravel, silt, and clay deposited as layers or lenses. Depending on the dominating fracture the aquifer can be more or less conductive and homogeneous.

One can distinguish such heterogeneity patterns as regular or random. Regular heterogeneity is formed by the layers as the vertical succession of deposits (sediments), changing the layer thickness in horizontal directions or by geological disturbances (faults) (Fig. 4.11,a). Random heterogeneity is formed by sporadic and irregular inclusions of various size and shape (Fig. 4.11,b).

Ground water flow in a heterogeneous rock changes directions at the boundaries between rocks with significantly different hydraulic conductivities (Fig. 4.12). Commonly flow lines change the angle depending on the relationship between conductivities except the case when flow lines are perpendicular to the boundary. Heterogeneity amplifies dispersion of contaminants in the aquifer due to enlargement of the scale of their transport. The shape of a contaminant plume is heavily dependent on rock heterogeneity.

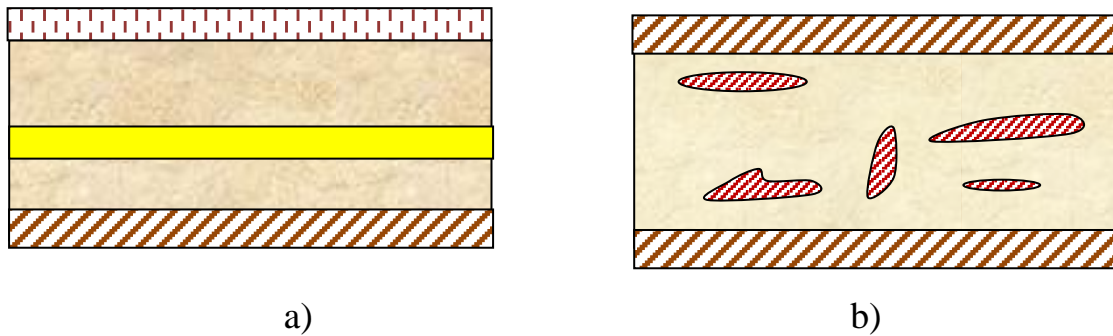


Fig. 4.11. Different kinds of aquifer heterogeneity: a) regular, b) random.

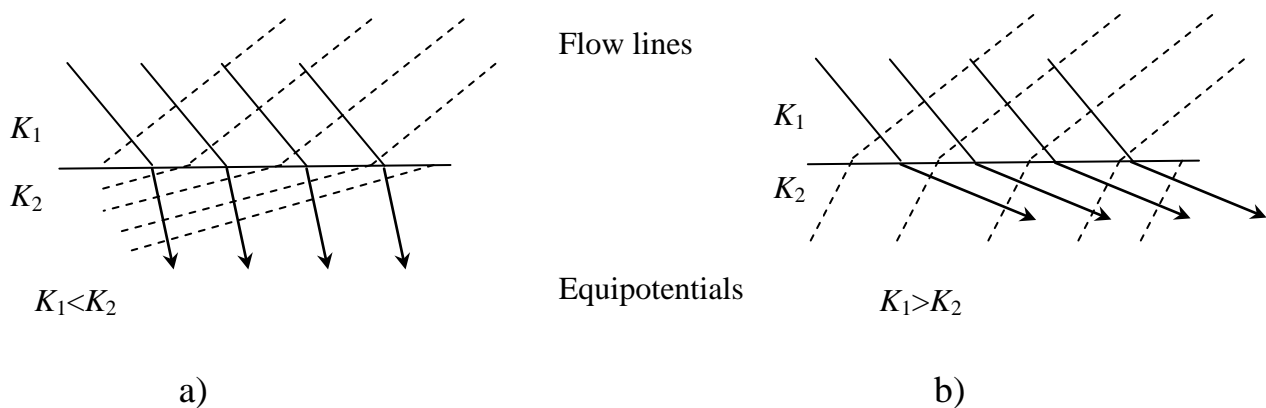


Fig. 4.12. Ground water flow at the boundary between two layers of different conductivity [37]: a) from less to more conductive material ($K_1 < K_2$), b) from more conductive material to that less conductive ($K_1 > K_2$).

The properties of consolidated deposits in aquifers may change in time due to compaction caused by withdrawal of significant water volumes. The hydraulic conductivity of karstified rocks may increase due to dissolution processes. These are specific cases of changing properties of geological materials in aquifers.

Fractured rocks. In many cases geological materials are characterized as low-permeable, for example, crystalline rocks. Nevertheless, they behave frequently as commonly permeable materials allowing significant discharge of water flow. In many regions of the world glacial-till aquifers are exploited with dug wells for local supplies. Often the productive wells are developed in metamorphic rocks and re-crystallized limestone. Additional fracturing of rocks may significantly increase the hydraulic conductivity with a small increase in porosity. The well-known example is “fracking” technology applied to extract shale gas.

A *fracture* is a planar discontinuity in a rock or cohesive sediment. Generally, it provides a path for water flow through rock. A *joint* is a type of fracture that forms near the ground surface [59]. Joints are mostly macro-fractures wide enough that one can stick a hand into a joint.

A single fracture is quantified by its attitude (orientation) in space, size, and aperture. A collection of fractures having approximately the same attitude in space is referred to as a set of fractures.

Anisotropy of rocks or soils can be defined as a change in the same property along spatial different directions. E. g., hydraulic conductivity of fractured rocks is significantly higher along the fracture directions and lower in the perpendicular direction (Fig. 4.13). Besides, conductivity of porous sediments may differ notably along and perpendicular the deposition direction. Fractured and karst aquifers are commonly more anisotropic than sandy aquifers due to extremely higher permeability in the zones of fracturing or soluble openings.

Anisotropy is caused by geologic processes including faulting, fracturing while cooling igneous rocks and bending planes, as well as sedimentation and metamorphism. As a result, the directions of anisotropy in rocks are not actually perpendicular to each other. Nevertheless, for simplicity in hydrogeological calculations and modeling three anisotropy axes are usually assumed mutually perpendicular and, moreover, parallel to the axes of the Cartesian coordinate system.

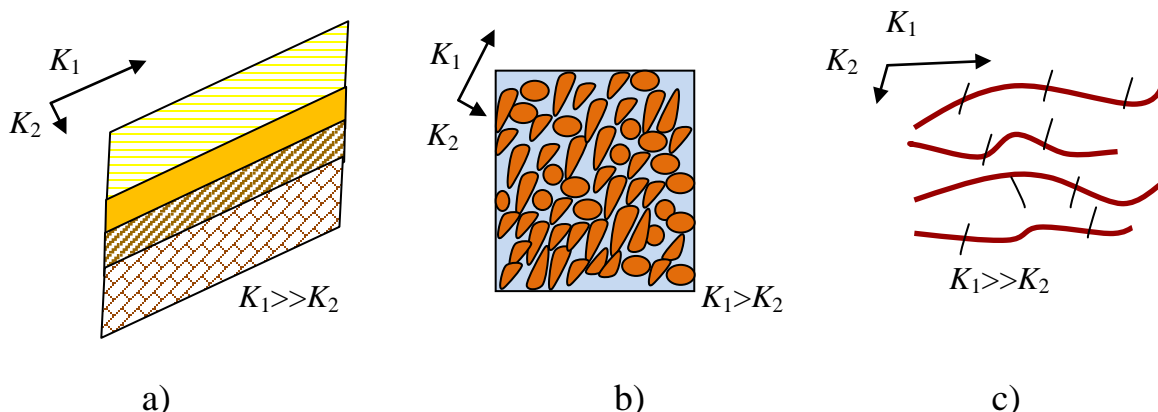


Fig. 4.13 Anisotropy in sedimentary layers (a), gravel deposits (b), and random heterogeneity in fractured rocks (c) (the sign “>>” means “much greater than”)

Generally, understanding the origins of heterogeneity and anisotropy of rocks and soils requires deep geological knowledge. In practice, to simplify calculations and provide computational feasibility hydrogeologists frequently assume only three or even two (vertical and horizontal) directions of anisotropy.

Section review

1. Characterize one of the geological materials (gravel, sand, silt, clay) in terms of total and effective porosity.
2. Explain how compaction, lithification, and sorting grains can change soil porosity.
3. Quantify the ranges of total and effective porosity for sedimentary soils and crystalline rocks.
4. Quantify the ranges of storativity and storage for sedimentary soils and crystalline rocks.
5. Explain the difference between storativity in confined and unconfined aquifer.
6. Compare static and dynamic storage of an aquifer.
7. Explain the difference between specific yield and specific retention.
8. Explain and illustrate the role of compaction in development of land subsidence.
9. What does aquifer mining mean and what are its after-effects? Give the examples.
10. How is the hydraulic head defined? Explain the difference between the hydraulic head and the ground water level.
11. Can ground water flow in the upward direction?
12. Give definitions of ground water flow lines and equipotential lines.
13. Which factors influence hydraulic conductivity of soils and rocks?
14. Quantify the ranges of hydraulic conductivity for sedimentary and crystalline rocks.
15. Does hydraulic conductivity depend on temperature? Why?
16. What are the ranges and units of intrinsic permeability of soils and rocks?
17. Does the term “transmissivity” characterize soils/rocks or an entire aquifer?
18. Explain why a thin aquifer may transmit more water than a thick one?
19. How is the effective grain diameter defined?
20. Compare the applicability of the empirical formulae for calculating hydraulic conductivity.
21. Explain the term “representative elementary volume”.
22. Characterize the major forms of soil/rock heterogeneity and their impacts on ground water flow.
23. Characterize the major forms of soil/rock anisotropy and their impacts on ground water flow.

5. GROUND WATER FLOW

5.1. Flow equations

Darcy's law. Water content in unsaturated soil. Water potential. Hydraulic conductivity of unsaturated soils.

Darcy's law. Henry Darcy worked as an engineer responsible for the public water supply in Dijon, France. In the mid of the XIXth century he explored how to improve the design of sand filters for purification of water. Darcy has conducted a number of experiments using an apparatus similar to that shown in Fig. 5.1.

His testing system was based on the cylinder of the known cross-sectional area A , which was filled with various sands. Appropriate sealing was provided to flow water through the column. Two manometers separated by a distance Δl were installed in the cylinder; they were small open tubes providing measurements of hydraulic heads. Water flowed into and out of the cylinder at a known rate Q , and the elevation of water levels in the manometer h_1 and h_2 was measured relative to local datum.

The experiments conducted for various types of filter materials and at different flow rate Q enabled deriving the relationship now known as *Darcy's equation* or *Darcy's law*.

$$\frac{Q}{A} = K \frac{h_1 - h_2}{\Delta l}, \quad (5.1)$$

where K is hydraulic conductivity. The term

$$q = \frac{Q}{A}, \quad (5.2)$$

representing the volumetric flow per unit cross-sectional area of the cylinder, is flow velocity (or Darcy's velocity or *specific discharge*). The Darcy's law states that the velocity of flow q is proportional to the hydraulic gradient i , or there is the linear proportionality between the flow velocity and hydraulic gradient.

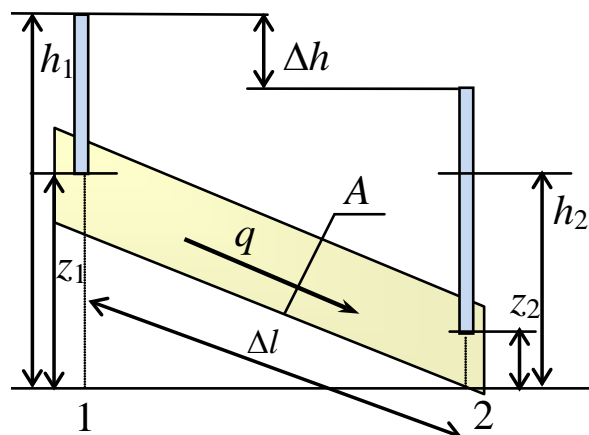


Fig. 5.1. Scheme of the apparatus to derive Darcy's law

This can be written as [59]

$$q = K i, \quad (5.3)$$

or

$$Q = K i A. \quad (5.4)$$

Darcy's law is valid for flow through most granular materials and applicable primarily to laminar flow. In case of turbulent flow the water particles move along tortuous paths. For low-permeable materials, like clays, seepage is possible only if hydraulic gradient exceeds a minimum non-zero threshold gradient i_0 or

$$q = K (i - i_0). \quad (5.5)$$

Thus, for turbulent ground water flow, primarily in gravel and some coarse sand sediment, as well as for seepage through low-permeable clays Darcy's law may give significant deviations from the real proportions between flow velocity and fluid discharge.

Darcy's law in the form of Eq. 5.3 or Eq. 5.4 assumes that flow occurs over the entire surface area of the soil column. Actually water flows through in pore space only, and the real flow velocity or pore velocity is greater than the specific discharge. The *pore velocity* or *linear velocity* v is defined as the volumetric flow rate per unit interconnected pore space

$$v = \frac{q}{n_e}, \quad (5.6)$$

where n_e is the effective porosity. The pore velocity is actual velocity of water flow in a porous material, whereas the specific discharge is the apparent velocity. In other words, the hypothetical tracer particle is moving in ground water at a pore velocity. Non-sorbed contaminants are transported with the linear ground water flow velocity.

Example. Calculate flow velocity and specific discharge for a uniform ground water flow head in two observation points A and B ($h_A = 120$ m, $h_B = 110$ m) at the distance of 200 m assuming hydraulic conductivity $K = 2$ m/day and effective porosity $n_e = 0,2$.

The hydraulic gradient

$$i = \frac{h_A - h_B}{L} = \frac{5 \text{ m}}{200 \text{ m}} = 2,5 \cdot 10^{-2},$$

then, specific discharge is calculated as

$$q = 2 \frac{\text{m}}{\text{day}} \cdot 2,5 \cdot 10^{-2} = 5,0 \cdot 10^{-2} \frac{\text{m}}{\text{day}}.$$

Water content in unsaturated soil. Prediction of water content in the unsaturated zone is the problem of growing importance regarding to various engineering applications in irrigation, drainage of agricultural lands and building foundations, percolation of contaminants in the topsoil after spills and releases from underground storages etc.

Commonly a large portion of pores in the unsaturated soil is filled with soil gases and the rest pore space is filled with a liquid. The degree of soil saturation with water is quantified in terms of *volumetric water content*

$$\theta_w = \frac{V_w}{V_s}, \quad (5.7)$$

where V_s is the volume of the soil, V_w is the volume of water.

The *water saturation* is defined as

$$\theta_s = \frac{V_w}{V_p}, \quad (5.8)$$

where V_p is the volume of pores.

As a rule, the volume of water in the unsaturated soil is less than porosity so that the volumetric water content is less than porosity ($0 < \theta_w < n$) so the water saturation is less than 1.

The relative water saturation $\bar{\theta}$ is defined as

$$\bar{\theta} = \frac{\theta - \theta_r}{\theta_{max} - \theta_r}, \quad (5.9)$$

where θ_r is residual water content, θ_{max} is the maximal water content of the soil. Residual water is defined as the water firmly associated with the soil grains and can be removed only by heating the soil sample over 105 °C. The relative water saturation is less than 1,0 and, multiplied by 100%, is expressed in per cents.

Water potential or suction pressure Ψ is formally defined by the work required to raise the unit weight of water to the equilibrium position in the system “soil-water” or, to the position of a water reservoir (Fig. 5.2). Water potential equals zero at the water level in the piezometer. Below this level in the saturated zone the pressure Ψ is always positive and equal to hydraulic pressure increasing in depth; above this position in the unsaturated zone the pressure Ψ (here suction pressure) is negative.

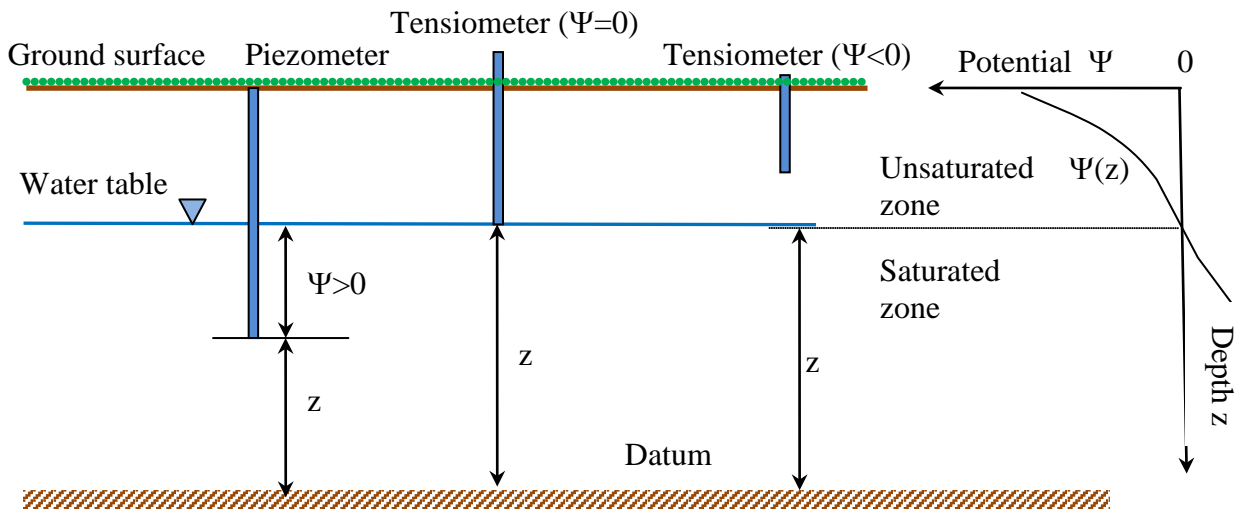


Fig. 5.2. Pressure in saturated and unsaturated soils [8]

Many factors contribute to the overall water potential Ψ as follows

$$\Psi = \Psi_s + \Psi_p + \Psi_{os} + \Psi_g + \Psi_h + \Psi_m, \quad (5.10)$$

where Ψ_s is the solute potential, Ψ_p is the pressure potential, Ψ_{os} is the osmotic potential, Ψ_g is the gravimetric (gravity) potential, Ψ_h is the humidity potential, and Ψ_m is the matrix potential. Commonly most important are matrix and gravitational potential.

The matrix potential is formed as a result of interaction between the fluid and solid phase (fluid cohesion and surface tension). In the saturated soil Ψ_m theoretically equals zero, but measurements show sometimes small negative values of the matrix potential even in the “saturated” soil.

The gravitational potential Ψ_g is the height difference between the point of observation and a point of reference and does not depend on soil properties. The reference level is chosen arbitrarily; thus, the only potential difference between two points is of practical interest.

Under isothermal conditions, water flows from the areas of higher water potential to the areas of lower potential. Consequently, water can flow in the direction opposite to the direction of gravity (e. g., in case of extensive evaporation when the water rises from the deeper and wet soil layer to the dry topsoil). Water in the unsaturated zone is actually driven by the water potential gradient instead of the humidity gradient (Fig. 5.2). Thus, the water potential is a continuous function of depth even in layered soils. However, there can be a noticeable difference in water content on the boundary between layers with different soil properties.

Hydraulic conductivity of unsaturated soils. The hydraulic conductivity K_u of unsaturated soil depends essentially on water content. Commonly K_u for the almost dry soil is several orders (10^3 – 10^4) less than the hydraulic conductivity of the same saturated soil. Thus, it is important for practice to determine the relationships between soil saturation, suction pressure, and hydraulic conductivity of unsaturated soil in the general form

$$\Psi = \Psi(\theta), \quad K_u = K_u(\theta). \quad (5.11)$$

Usually the empirical formula (Table 5.1, Fig. 5.3) or data in tabular form [61] are applied. Due to hysteresis these formulae may differ for the cases of wetting and drying, although quantifying this effect needs accurate measurements.

Water flow in unsaturated soil is governed by the analogue of Darcy's law for a saturated soil [4, 61]

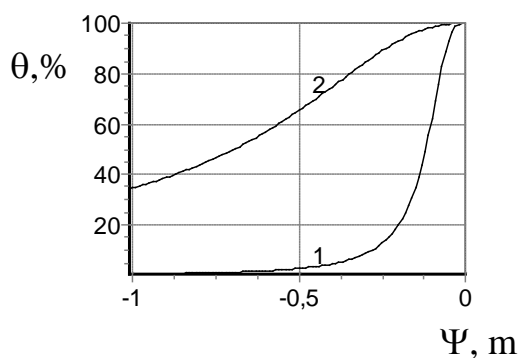
$$v_u = K_u \text{ grad } \Psi, \quad \Psi = \frac{\Psi_\Sigma}{\rho g} + z, \quad (5.12)$$

where v_u is unsaturated flow velocity; K_u is the unsaturated hydraulic conductivity, Ψ is the total water potential, Ψ_Σ is the total water potential except the gravity potential.

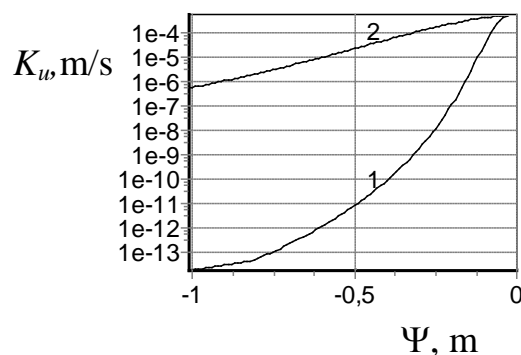
Table 5.1

Empirical formulae to calculate unsaturated conductivity [4]

#	Author	Formula	Clarifications
1	Irmay, Averianov, Collis-George Childs	$K_u = K \bar{\theta}^p$	The formula can be applied to homogeneous soil; $p = 3$ (Irmay), $p = 3.5$ (Averianov)
2	Gardner	$K_u = K \frac{a}{(b + \Psi ^m)}$	a, b are fitting parameters, $m = 2$ for heavy clays, $m = 4$ for sand. For a saturated soil ($\Psi = 0$), $K = a/b$
3	Gardner	$\bar{\theta} = \exp(-\alpha(\Psi + \Psi_\alpha))$, $K_u = K \exp(-\beta(\Psi + \Psi_\alpha))$.	$\alpha, \beta, \Psi_\alpha$ are fitting parameters. Sometimes these formulae disagree to experimental data model but feasible for computation
4	Mualem – Van- Genuchten	$\bar{\theta} = [1 + \alpha\Psi ^n]^m$, $K_u = K \sqrt{\bar{\theta}} \left[1 - \left(1 - (\bar{\theta})^{\frac{1}{m}} \right)^m \right]^2$	The formulae takes into proper account pore geometry and void saturation in soil. α, n, m are fitting parameters, $m = 1 - 1/n$



a)



b)

Fig. 5.3. Change in soil saturation (a) and hydraulic conductivity (b) versus suction pressure calculated by Mualem – Van-Genuchten formulae for coarse-grained material (1) and fine-grained sand (2)

5.2. Initial and boundary conditions

Initial conditions. Boundaries of ground water flow. Boundary conditions of the first, second, third, and fourth kind. Time-dependent boundary conditions.

Initial conditions are the term that denotes the spatial distribution of ground water head (or water pressure) in the aquifer system at a starting time moment for a transient (time-dependent) flow. The initial ground water distribution is the result of

hydrogeological development and boundary conditions having acted before during a certain period of time.

In principle, the results of field measurements of ground water head in the set of wells and other observation points could be the initial conditions for ground water flow. More strictly, initial conditions have to be close to the equilibrium state of an aquifer system before any natural or man-made disturbance occurred that changed the existed ground water head distribution. Frequently, due to the lack of field data there are the difficulties in evaluating the initial ground water heads that are often defined using interpolation in space and time.

Initial conditions are often available in the form of contour maps of water table or hydraulic heads (Fig. 5.4). Contour maps properly built and drawn provide important information on ground water flow and enable calculating hydraulic gradients, flow rates and velocities, evaluating aquifer properties (conductivity and transmissivity). There are difficulties in mapping hydraulic head or water level in karst or fractured aquifers in small scale because of flow discontinuity effects near fissures, fractures, and karst openings allowing considerable amounts of ground water to flow in narrow zones. Enlarging the scale can facilitate mapping of ground water flow in the same aquifers owing to minimization of heterogeneity scale.

If a three dimensional aquifer system consists of several hydrogeological units, then initial conditions have to be set, at least, for each permeable unit. Commonly low-permeable beds do not require setting the initial conditions, which is, moreover, hardly feasible for technical reasons (measurement of hydraulic head in clay deposits).

Boundaries of ground water flow are defined as the surfaces where water enters or leaves the aquifer system. Commonly there are three types of ground water flow boundaries that are (1) known head, (2) known flux, and (3) head-dependent flux (Fig. 5.5).

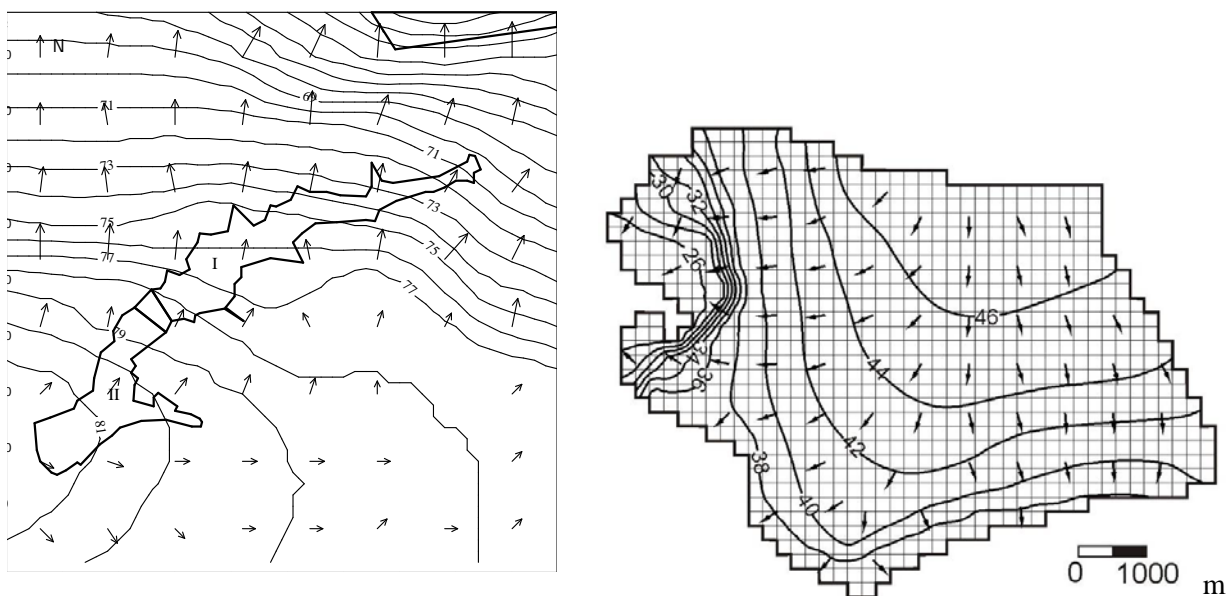


Fig. 5.4. Initial conditions in forms of equipotentials [56]

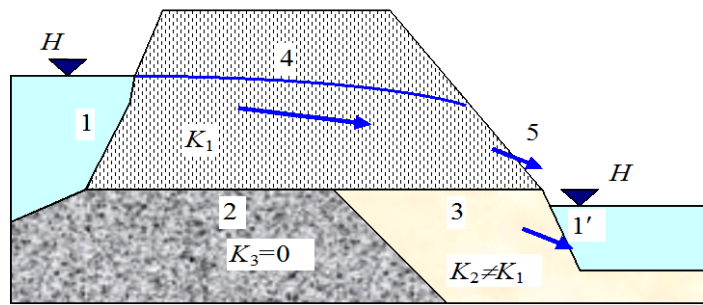


Fig. 5.5. Boundary conditions for ground water flow [4]:

1 – contact between surface water and ground water, 1' – subsurface runoff boundary, 2 – almost impermeable boundary (“no-flow” boundary), 3 – boundary between two layers of different permeability, 4 – ground water table where water pressure is equal to atmospheric pressure. 5 – seepage face.

These conditions are assigned to the boundaries that can be classified as either external or internal depending on location and the scale of the system. The water table in an unconfined aquifer that receives infiltration water as a known or estimated recharge (flux) could be the example of an external boundary. A big river fully contacted by an aquifer is another example of the external boundary with the known head that is the same as the water level in the river.

A well with the recorded pumping rate is the example of an internal boundary with the known flux. Another example of an internal boundary is the boundary between two layers, one of them is the aquifer and the other is the aquitard. In this case the flux between the layers is unknown and has to be determined

Boundary conditions of the first, second, third and fourth kind are defined in numerous books including [4, 5, 36, 59]. The first kind boundary condition (known head) is commonly set on the direct contact between the aquifer and a surface water body that is not divided by sediments. In this case the water level in the aquifer can be set on the aquifer boundary as the ground water head. This boundary condition is applicable to the aquifers bounded by the sea coast, the beach of a deep lake or river.

The boundary condition of the second kind is set on the boundary as a known flux. The most simple and frequently occurring example of such boundary is the water divide or aquiclude called also “no-flow” or “zero-flux” boundary through which water does not flow or water flux equals zero. Water does not flow through the divide in horizontal direction but downward percolation can occur. Similarly, vertical flow through aquiclude does not occur, however, ground water flows in mostly horizontal directions in the aquifer with some deepening to the aquitard slope.

The springs flowing from the slope to the surface water body could be also the example of the boundary with known flux. However, sometimes it is difficult to estimate this flux directly; alternatively, the known head can be set at this boundary at the position somewhat higher the contour of springs occurrences.

Commonly the values of water flux on the boundary are difficult to assign using field measurement of ground water velocity. Then, the flux can be evaluated indirectly but not assigned, for example, the recharge rate on the ground water surface of the shallow aquifer.

The most general is the boundary condition of the third kind. Commonly, if the river is hydraulically connected with an aquifer as shown in Fig. 5.5 the flux-dependent head is set on such a boundary. This condition relates the flux through the boundary with the difference between the water level in the river and ground water head multiplied by the hydraulic conductance (transmissivity) of riverbed sediments. If the conductance of sediments is low, the hydraulic contact between ground water and surface water body is insignificant, so the boundary tends to be the “no-flux” boundary. If the conductance of sediments is high, there will be no significant hydraulic resistance between ground and surface water; thus, this boundary tends to be the first-kind boundary with the set ground water head.

The contact surface between two layers of different properties (conductivity and porosity) is a specific kind of an internal boundary where the condition of the fourth kind is set. This condition means that hydraulic heads on both sides of the boundary surface are equal, the flux entering one layer equals to that leaving the other layer. This condition refers to heterogeneity and anisotropy described in Section 4.

In case there is no sufficient information to define a boundary or to set a boundary condition two options are possible. For remote contours the “no-flow” condition can be set, which requires thorough positioning of the boundary that must not be reached by any hydraulic disturbances during the certain period. Otherwise, this boundary can be represented by the known ground water head assigned regarding the actual hydraulic gradients. The main problem of this interpretation is the following. If ground water head sinks, the flux of water entering the aquifer through the boundary will increase. Consequently, the hydraulic gradient and head on the boundary will change, which is not taken into account in the boundary condition with constant head.

To contour the aquifer boundaries the water budget should be defined beforehand. The sum of water in- and outflows has to be equal to the change in water storage inside the aquifer system. The water flux has to be assigned on the known-flux boundaries; in contrast, in case of the known-head and flux-dependent head boundaries the flux is calculated using hydraulic heads and conductance during computations.

Time-dependent boundary conditions. The parameters of boundary conditions may change in time due to seasonal fluctuations of the water level in rivers, lakes, and seasonal changes of infiltration as well as underground mining, construction and installation of drains. Moreover, the kind of boundary condition may also change due to these factors. This is important for transient (unsteady) flow but can be neglected for simplified steady-state ground water flow.

Boundary conditions can vary in time depending on natural factors. E. g., recharge on the ground water level of the unconfined aquifer changes due to seasonal variations of infiltration. Pumping rate may change in time due to the schedule. The

water level in a pond, lake or river can change as a result of strong rains followed by flood, severe drought, mining activities or drainage.

Moreover, some boundaries may even appear or disappear for various reasons. Many rivers in arid zones are temporary and exist only after strong rains like “wadis” in Near East and Arabian Peninsula or small rivers with the sinking water level in summer in semi-arid zones of Asia and North America.

Section review

1. Clarify the physical sense of Darcy’s law.
2. Describe the applicability and limitations of Darcy’s law.
3. Are fluid particles moving in ground water flow at flow velocity or linear velocity? Which velocity is higher?
4. Explain the differences between volumetric water content and water saturation.
5. What are the constituents of the overall water potential?
6. Clarify the physical sense of suction pressure.
7. Explain the conditions of upward flow in the topsoil.
8. How does the unsaturated conductivity change if soil is saturated or dried?
9. Clarify the terms “initial conditions” and “boundary conditions”.
10. What are the sources of uncertainties in initial and boundary conditions of ground water flow?
11. Give the example of the first kind boundary? What parameter(s) has/have to be given on this boundary?
12. Give the example of the second kind boundary? What parameter(s) has/have to be given on this boundary?
13. Give the example of the third kind boundary? What parameter(s) has/have to be given on this boundary?
14. Explain the difference between the external and internal boundaries.
15. Give the examples of a “no-flow” boundary.
16. Identify a river with the varying water level as the boundary of ground water flow (kind of boundary condition, internal or external boundary).
17. What conditions have to be set on a remote boundary?
18. Identify a drain and a well as the boundary of ground water flow (kind of boundary condition, internal or external boundary).
19. Explain the condition on the boundary between two layers of different conductivity.

6. GROUND WATER CHEMISTRY

6.1. Species in ground water

Concentration scales. Chemical composition of ground water. Ground water ionic composition. Hydrogen-ion activity (pH) and redox potential. Water analyses.

Concentration scales. Rocks and minerals can dissolve in water and form ions. *Cations* are positively charged species, such as Ca^{2+} or K^+ , *anions* are negatively charged species, such as HCO_3^- or Cl^- .

Organic substances can also dissolve and form organic cations or anions. However, most organic compounds, including that are artificial (trichlorethene or TCE) dissolve as nonionic or uncharged molecules. Ions of organic molecules turn up in water as a result of dissolution of minerals, for example,



The amount of a substance in a ground water volume is quantified in such scales as molar, molal, equivalent charge, and mass concentrations [59].

Molar concentration denoted by M or mM or μM is the number of moles of a species per liter of solution and is measured in mol/L. A mole is the formula weight of a substance expressed in grams. For instance, a one liter solution containing 1 g of KCl has a (KCl) molarity of $\frac{1}{39,1 + 35,45} = 0,013 \text{ M}$. As KCl dissociates completely

in water the molar concentrations of K^+ and Cl^- are also 0,013 M. In this reaction one mole of KCl dissolves to produce one mole of K^+ and one mole of Cl^- .

Molal concentration is the number of moles of a species per a kilogram of solvent and measured in mol/kg. For solutions with small amount of species or dilute solutions this scale of concentrations is almost the same as molar concentrations because a one liter solution has the mass of approximately 1 kg. However, these scales become different for more concentrated solutions, especially brines of concentration greater than 100 g/L.

Equivalent charge concentration is the number of equivalent charges of an ion per liter of solution; it is measured in eq/L or meq/L. The equivalent charge of an ion is equal to the number of moles of an ion multiplied by the absolute value of the charge. For example, with a singly charged species like Na^+ , 1 M Na^+ equals 1 eq/L; with a doubly charged species like Mg^{2+} 1 M Mg^{2+} equals 2 eq/L.

Mass per unit mass concentration is the mass of a species or element per total mass of a system. Previously, many analyses were documented using this parameter expressed in parts per million (ppm), later these units of concentrations were often expressed in mg/kg.

Mass per unit volume concentration is the most common in various ground water applications. It defines the mass of solute dissolved in a unit volume of solution. Concentrations are measured in mg/L or µg/L (microgram/L). There is a close correspondence between the last two types of concentration. For dilute solutions 1 ppm is approximately equal to 1 mg/kg or 1 mg/L.

The various concentrations can be converted using these formulae:

$$\text{molarity} = \frac{\text{mg/L} \times 10^{-3}}{\text{formula weight}}, \quad (6.1)$$

$$\text{meq} = \frac{\text{mg/L}}{\text{formula weight/charge}}. \quad (6.2)$$

Example. Convert the concentration 85 mg/L of SO_4^{2-} in water solution into molarity and meq/L. Substituting atomic masses of sulfur and oxygen to Eqs. 6.1 and 6.2 yields

$$\text{mol/L} = \frac{85 \cdot 10^{-3} \text{ mg/L}}{32,06 + 4 \cdot 16,0} = 0,89 \cdot 10^{-3},$$

$$\text{meq/L} = \frac{85 \text{ mg/L}}{(32,06 + 4 \cdot 16,0)/2} = 1,77.$$

In the following table the concentration of ions in water is expressed in mg/L. Convert this concentrations in molarity and meq/L.

	1	2	3	4	5	6	7
Ion	SO_4^{2-}	Cl^-	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Concentration, mg/L	250	30	150	120	250	500	50

Chemical composition of ground water. Water in subsurface contains minerals and organic solids both soluble and suspended, organic liquids, and gases. Inorganic compounds are classified as major constituents with concentrations greater than 5 mg/L, minor constituents with concentrations from 0,01 to 10 mg/L, and trace elements with concentrations less than 0,01 mg/L (Table 6.1). The natural organic compounds in ground water are large in number and typically present at low quantities. The most abundant organic compounds in shallow ground water are the humic and fulvic acids.

Content of dissolved solids in ground water is also called total salinity or *TDS* (*total dissolved solids*). TDS is commonly determined by weighing the dry residue after heating the water sample, usually to 103 or 180 °C.

Ground water is classified by its total salinity as shown in Table 6.2. The water of the salinity greater than 50 g/L is often called brine. The most concentrated brines of salinity up to 600 g/L or higher have been found in ancient salt deposits in Eastern Siberia [10]. For instance, 1 L of brine from the Omoloyska well contains 626 g of salts (chloride of calcium and magnesium). The mass of salts in this brine is almost equal to the mass of water as solvent. Ground water of extremely low salinity (below 0.1 g/l) is typical for mountainous areas.

Table 6.1

The dissolved constituents in ground water [7, 59]

Major constituents	Bicarbonate, calcium, chloride, magnesium, silicon, sodium, sulfate, and carbonic acid
Major constituents	Boron, carbonate, fluoride, iron, nitrate, potassium, strontium
Trace elements	Aluminum, antimony, arsenic, barium, beryllium, bismuth, bromide, cadmium, cerium, cesium, chromium, cobalt, copper, gallium, germanium, gold, indium, iodide, lanthanum, lead, lithium, manganese, molybdenum, nickel, niobium, phosphate, platinum, radium, rubidium, ruthenium, scandium, selenium, silver, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, ytterbium, yttrium, zinc, zirconium
Organic compounds	Humic acid, fulvic acid, carbohydrates, amino acids, tannins, lignin, hydrocarbons (shallow ground water) Acetate, propionate (deep ground water)

Table 6.2

Natural water classification in terms of salinity

Classification	Natural occurrences	TDS range
Extremely fresh water	Mountainous lakes and rivers	Less than 0,2 g/L
Fresh water	Inland rivers and lakes	0,2–1,0 g/L
Brackish water	Coastal aquifers, lakes and rivers in arid climate	1,0–3,0 g/L
Salt water	Seas, oceans, deep aquifers	3,0–50,0 g/L
Saline water, brine	Dead Sea, deep aquifers	Greater than 50,0 g/L

There are two main sources of salt accumulation in ground water; the first is leaching of rocks, the second is evaporation and concentration. The most intensive evaporation occurs from the shallow aquifer and unsaturated zone in arid climate. Under some conditions minor constituents may be present at higher concentrations and even become a primary constituent in ground water. For example, silica acid is often the major constituent in ground water of very low salinity in northern areas. Carbonate ion CO_3^- is found only in alkaline water.

Bromine, iodine, fluorine, boron, strontium, barium, and some other elements are widespread in ground waters. Their content in deep aquifers often reaches

hundreds of milligrams per liter. Heavy metals are usually in waters at very low concentrations, some hundredths and thousandths of a milligram per liter. However, in water near metal ore deposits heavy metal concentrations increase dramatically.

Ground water contains organic matter everywhere in concentrations ranging from tens to hundreds of milligrams per liter. Various organic compounds (hydrocarbons, organic acids, etc.) come into ground waters as a result of interaction with oil-bearing rocks in oil deposits, leaching of rocks, and biochemical processes.

The important gases in ground water are oxygen, carbon dioxide, hydrogen sulfide, and methane; in various locations there are also dissolved nitrogen, hydrogen, helium, radon, and others. These gases may enter rocks from air, can be produced as a result of biochemical reactions, metamorphic or magmatic processes. Helium and radon are emitted during radioactive decay.

Solubility of gases in ground water increases with increasing pressure and depth, but it decreases with increasing temperature. Water of deep aquifers often contains several hundred cubic centimeters of dissolved gas per liter in normal conditions. Gas and ion compositions of ground waters are closely related to each other. Increasing concentration of dissolved salts leads to decreasing solubility of gases; lowering the gas content in water affects solubility of salts and their precipitation.

Ground water like other components of the hydrosphere has its dissolved “atmosphere”. Water in the active circulation zone usually contains oxygen and nitrogen involved in gas exchange with atmosphere and soil, and some quantities of carbon dioxide [10]. Hydrogen sulfide and methane appear in deeper aquifers. Besides, deep ground water often contains a lot of carbon dioxide, and often hydrogen, its content reaches tens, and sometimes, even thousands of cm^3/L .

Dissolved gas content in ground water can be very large because of the increase in gas solubility when pressure increases. Gas content in ground water within the depth range from 1 km to 4 km may be of $500 \text{ cm}^3/\text{L}$; water with $1000\text{--}1500 \text{ cm}^3/\text{L}$ of gas has been detected in some Western Siberia areas, whereas ocean water contains on the average only $20 \text{ cm}^3/\text{L}$ of dissolved gas [10]. The total mass of gases dissolved in ground water is likely to be approaching the mass of gas dissolved in oceans, and being close to the mass of gas in the atmosphere.

There are zones in saturated rocks with prevailing oxidizing conditions typical for active water circulation and anoxic (reduction) conditions typical for slow and passive water circulation in deep aquifer systems.

Chemical composition of ground water is the result of various natural factors and phenomena. The origin of ground water, its velocity, nature of water-bearing rocks and soils, temperature, and pressure as well as other conditions affect ground water composition. Commonly, a clear vertical hydrochemical zonation occurs; with increasing total salinity of ground water and change of chemical composition in depth. However, some deep aquifers contain water of lower salinity than those lying above due to slow water exchange below and hydraulic connections of shallow aquifers with surface waters of higher salinity.

Chemical composition of ground waters is also closely dependent on various geological processes including seismic activity. Concentration of some compounds in

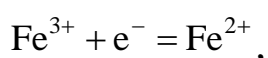
water can vary as a result of earthquakes, which can be an indicator of coming earthquakes.

Ground water ionic composition. The overwhelming majority of salts exist in aqueous solutions as ions. In natural waters there are three major anions [35] that are bicarbonate HCO_3^- , chloride Cl^- , and sulfate SO_4^{2-} ; there are four major cations, which are calcium Ca^{2+} , magnesium Mg^{2+} , sodium Na^+ , and potassium K^+ ; all ions are referred to primary ions. Chloride ions give a salty taste to water, sulfate, calcium, and magnesium ions give the bitter taste to water, and hydrocarbon ions are tasteless. These ions constitute over 90% of salts in freshwaters and over 99% in highly concentrated solutes. Typically, the lower limit for the major ion concentration is considered to be 1 mg/L. Thus, in some cases, Br^- , B^{3+} , and Sr^{3+} may be referred to major cations of some ground water. For the same reason, potassium may not be referred to the major cations for some waters.

Dominating combination of ions in solutions determines the chemical type of ground water. Calcium bicarbonate water is very common. The brines of mid concentration are usually of sodium chloride type, more concentrated brines are of chloride, calcium and magnesium types.

Hydrogen-ion activity (pH) and redox potential. Hydrogen-ion activity is the best-known chemical characteristic of water. Water molecules dissociate into hydrogen ions H^+ and hydroxyl ions OH^- . By convention, the content of hydrogen ion in water is expressed in terms of its activity. The index *pH* is formally defined as the negative logarithm of the hydrogen ion activity. When the number of hydrogen ions equals the number of hydroxyl ions, the solution is assumed neutral, and hydrogen-ion activity, or pH, equals 7. When there are no hydrogen ions, the solution is alkaline and $\text{pH} = 14$, when there are no hydroxyl ions, the solution is acid and $\text{pH} = 0$. When the concentration of hydrogen ions decreases, the activity of hydroxyl ions must increase.

Reduction/oxidation can be defined as a gain/loss of electrons. An oxidizing agent is any material that gains electrons, a reducing agent is any material that losses electrons. In the reaction



iron gains one electron and is reduced.

The electric potential of a natural electrolytic solution with respect to the standard hydrogen half-cell measuring instrument is expressed in millivolts (mV), called *reduction-oxidation potential* or *redox* and denoted with *Eh*. Observed values of *Eh* for ground water range from -400 mV to $+700$ mV. The positive sign indicates that solution is oxidizing, the negative sign that solution is reducing. This parameter, like pH, should be measured in the field to avoid chemical reactions changing these indexes. A presence of H_2S greater than 0,1 mg/L produces negative *Eh* of a solution, the presence of oxygen in concentration greater than 1 mg/L results in positive values of *Eh* between $+300$ mV and $+450$ mV.

Water analyses. *Routine water analysis* involves measuring the concentration of a standard set of the most abundant constituents. The test results are the basis for making decision on suitability of analyzed water for human consumption or various

industrial and agricultural activities. Commonly, routine analysis includes the major constituents except silicon and carbonic acid, and some minor constituents, as well as some specific indexes like pH or TDS (Table 6.3) [59].

Table 6.3

Example of a routine analysis

Parameter	mg/L	Parameter	mg/L
pH	7,4	Conductivity	2240
Calcium	15	Magnesium	1
Sodium	530	Potassium	3,4
Iron	4,3	Nitrite	less than 0,1
Sulfate	50	NO ₂ , NO ₃	less than 0,1
Bicarbonate	1290	Chloride	43
Alkalinity, <i>T</i>	1010	Fluoride	0,23
TDS	1310	Hardness, <i>T</i>	7,9
Balance	1,01		

Alkalinity and hardness are expressed as calcium carbonate.

Routine analysis can be carried out quickly at low costs, often in the field. In many environmental-focused applications there is the need for more detailed analysis to examine the concentrations of trace elements or some specific compounds (radionuclides, organic compounds, or gases). This can be performed by specialized analysis only in laboratories, because it requires much more time and efforts than routine analysis.

6.2. Ground water contaminants

Significance of ground water contamination. Sources of contamination: fuel storage practices, waste disposal practices, agricultural activities, industrial activities, mining operations. Contamination through wells. Natural ground water contaminants. Synthetic organic contaminants. Nitrate, fertilizers, pesticides, concentrated animal feeding operations. Microorganisms and organic compounds. Silver nanoparticles. Drinking water standards.

Significance of ground water contamination. Any water containing disease-causing or toxic substances is defined as contaminated [48, 52, 75]. All sources of contamination can be grouped into two major categories: naturally occurring and of artificial (anthropogenic) origin. Some natural contaminants, like arsenic or uranium,

may have local or regional impacts on ground water supply; however, synthetic compounds affect the ground water quality much more significantly.

The rapidly developing analytical techniques of detecting various compounds in water solutions enable revealing the growing number of many synthetic organic contaminants. They are widely spread in ground water and can be found in human tissue and organs of people in all continents. Many people are ready to pay more for high quality water at least for drinking. Therefore, domestic and multinational companies are looking for ground water resources that can be marketed as “pure spring water”.

Ground water contamination is most common in developed urban, industrial, and agricultural areas. Frequently ground water contamination is discovered long after it has occurred. The main cause is slow movement of ground water often estimated at several meters per month. Secondly, some compounds could not be detected earlier due to insufficient capabilities of analytical equipment.

Sources of contamination. Ground water contamination can occur as localized plumes near point sources like leaking underground storage tanks, spills, landfills, waste lagoons, and industrial facilities [5, 16]. Nonpoint sources refer to a diffuse pollution discharged over a large area, not from a specific location; they include pollution caused by sediments, nutrients, organic and toxic substances originated from agricultural activities and urban development. Rainwater, snowmelt, and irrigation can wash out these substances from soils and carry them with runoff to surface streams and water intakes.

The most important sources of ground water contamination are (1) fuel storage practices, (2) waste disposal practices, (3) agricultural activities, (4) industrial activities, and (5) mining operations (Fig. 6.1) [37].

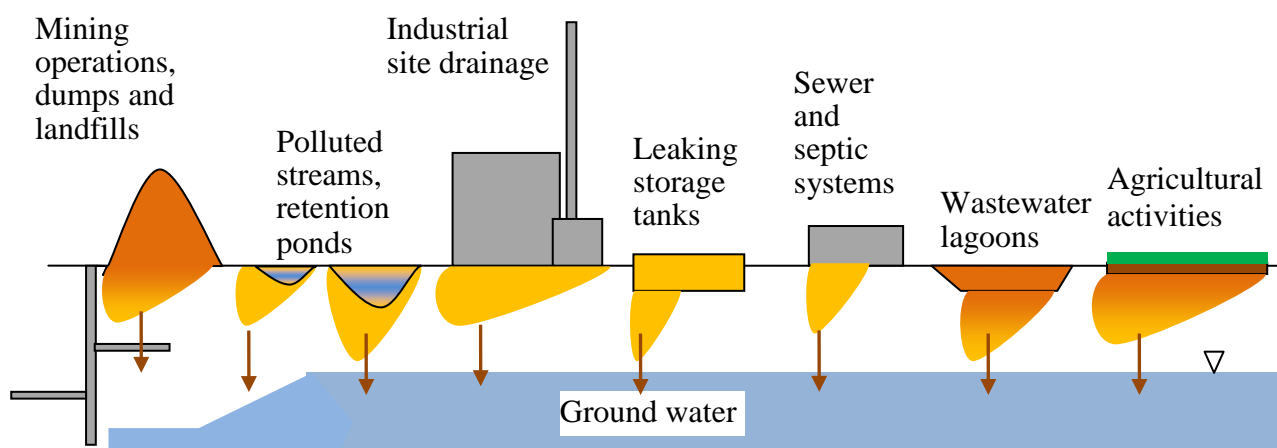


Fig. 6.1. Land use activities commonly generating ground water pollution

Fuel storage practices include the storage of petroleum products in underground and on-ground storage tanks. Usually an underground storage tank has at least 10% of volume below ground; these tanks are concentrated commonly in urban and industrial areas.

The primary causes of tank leakages are improper installation or corrosion. According to the data of US EPA by 2000 [75] about 18% of 85 000 inspected underground storages in the country had releases adversely affected ground water quality. Petroleum products are the mixtures of many different components mostly soluble in water and threatening the human health like benzene that is known to cause cancer at very low concentrations.

Waste disposal practices include septic systems, landfills, surface impoundments, deep and shallow injection wells, dry wells, sumps, waste tailings, and illegal disposal. The typical contaminants for those practices are metals, volatile organic compounds (VOCs), nitrates, radionuclides, and pathogens. In many cases the present-day ground water contamination is the result of previous practices at waste disposal sites.

Domestic or centralized septic systems for on-site sewage disposal are constructed using various designs. Conventional individual septic system includes a septic tank for detaining wastes; the liquids are infiltrating into the shallow unsaturated soil and being adsorbed. Improperly constructed and poorly managed septic systems cause widespread nutrient and microbial contamination of ground water. Nitrate contamination by individual septic systems and municipal sewage lagoons is a significant ground water contamination in many countries of the world. All sewage wastes contain various pharmaceuticals and personal care products (PPCPs) continuously released to the environment including ground water. Some of pharmaceuticals are very persistent and remain unchanged long time in ground water.

Landfills have been long used for waste disposal; however, earlier the risk of ground water contamination was not often taken into consideration. Unlined abandoned sand or gravel pits, old mines, marshlands, and sinkholes were used without protective bottom screens. Commonly the screens are made of concrete, low-permeable clays, and polyethylene films or their combinations; their conductivity ranges from 10^{-4} m/day to 10^{-8} m/day [18], in fact, there are no impermeable screens. Therefore, environmental authorities consider landfills as a highly dangerous source of ground water contamination. Now many efforts are being focused on improving the safety of landfills and tailings created prior to establishment of stringent standards to which modern facilities must adhere.

Impoundments are also the source of ground water contamination especially if they are located over thin or permeable confining beds overlying aquifers. Especially serious problems were caused by surface impoundments in limestone terrains with extensive near-surface solution openings. Liquid waste sewage lagoons and mine water ponds were collapsed into sinkholes draining an entering fluid into underground openings. Frequently leaked water has reappeared in springs and streams several kilometers away downstream in ground water flow.

Injection wells are used to dispose liquid wastes below the ground surface, to shallow or deep aquifers. Shallow disposal wells include “dry” wells, sumps, septic

systems, storm water drains, and agricultural drains. Deep injection wells are used in many countries to dispose waste fluids including those from municipal treatment plants, and landfill leachate. Because of improper well construction, well failure, or specific hydrogeological conditions deep injection wells may lead to upward transportation of contaminants and contamination of aquifers used for water supply.

Oil field brine is a by-product of oil extraction as well as drilling boreholes. As a rule, drilling fluids and brines are stored in reserve pits filled after completion or abandonment of the well. Oil field brines are stored in special tanks or placed into the injection wells. Owing to chemical activity of the brine, transporting pipelines and casings of injection wells can corrode, which results in ground water contamination.

Agricultural activities that contaminate ground water include animal feedlots, fertilizer and pesticide applications, irrigation, agricultural chemical facilities, and drainage wells. Ground water contamination can be a result of routine applications, spillage or misuse of pesticides and fertilizers during handling and storage, manure storage and spreading, improper storage of chemicals, and irrigation return drains that are actually conduits to aquifers [23, 75]. Now agricultural activities continue to be a major source of ground water contamination.

Concentrated animal feeding operations, where animals are kept and raised in confined spaces, occur in many countries. Such operations can pose significant risks to water quality and public health. Livestock waste contains nitrate, bacteria, and sulfides; these substances infiltrate into ground water from feedlot impoundments. For this reason, shallow unconfined aquifers in many countries are contaminated.

Pesticide application is of growing concern for ground water quality around the world. Pesticides are transported to ground water through unsaturated zone due to leaching in soil or directly infiltrate through drainage facilities. Pesticide infiltration depends on the rainfall rate and intensifies shortly after they are applied.

Extensive or improper irrigation may cause increased salinity of ground water, especially in the areas of high evaporation. Irrigation water flushes nitrate-related compounds from fertilizers to shallow aquifers, along with high levels of chloride, sodium, and other compounds. In the presence of permeable zones in the aquitard these contaminants may penetrate underlying aquifers. Improper irrigation can cause extensive soil salinization by raising the water table above the critical depth of evaporation; this process results in precipitation of dissolved salts and their accumulation at and near the ground surface.

Industrial activities pose significant risk to ground water quality, especially while processing raw materials and handling wastes. Releases of hazardous substances are possible from various industrial facilities, manufacturing and repairing shops, storages, transportation facilities (railways, aircrafts), chemical drums as a result of improper exploitation or damage. For example, in the USA hundreds of sites require extensive cleanup and follow-up ground water monitoring [75]. The leaks from many-kilometer long pipelines transporting various petroleum products and industrial fluids have serious risk to ground and surface water quality because these leaks are difficult to detect and stop in time. Sometimes they are disclosed or revealed suddenly due to deterioration of natural water quality and dying vegetation.

Atmospheric pollutants generated by power plants, various industries, vehicle emissions (predominantly sulfur and nitrogen compounds), fall as dry particles or acid rains on the land surface and infiltrate into soils and may cause diffuse ground water contamination.

Development of new technologies and products to replace synthetic solvents is continuing to grow, for example, new organic biodegradable compounds have been derived from plants recently. New organic solvents can reduce the need for highly toxic perchloroethylene (PCE) commonly used in dry cleaners.

Mining operations can result in a variety of water contamination caused by pumping mine water to the surface, leaching of material, water discharged to the mine, waste rock heaps and tailings. Thousands of square kilometers of aquifers have been contaminated by highly corrosive mineralized water originated from deep mine excavations and pits worldwide. Mill wastes and leachates from metal sulfide operations adversely affected surface and ground water near exploited deposits of non-ferrous metals.

To keep mines dry large quantities of water are pumped and discharged to impoundments for temporal storage and, in many cases, directly to streams and rivers. If salty or mineralized water occurs in relatively shallow depth, pumping of freshwater for dewatering may cause an upward migration partially intercepted by pumping wells.

Contamination through wells. Improperly operated, abandoned, uncased, and failed wells, or wells with long screens and gravel packs open to several aquifers may also contaminate ground water. Contamination is caused by dissolved compounds or water of different density depending on the differences in hydraulic head of the over- and underlying aquifers in the ground water system. For example, pumping from the overlying aquifer leads to falling pressure, which creates the hydraulic gradient directed upwards and upward migration of deep mineralized water (Fig. 6.2).

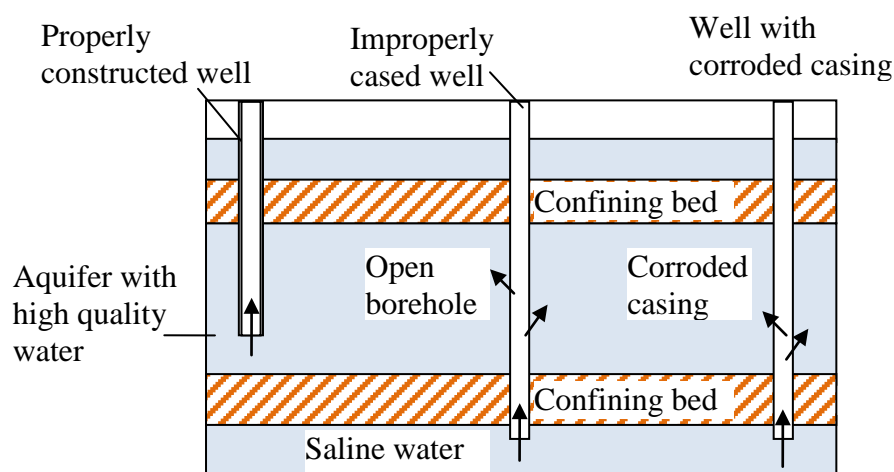


Fig. 6.2. Contaminant transportation between aquifers through wells (modified from [5, 40])

Natural ground water contaminants include naturally occurring chemical elements (arsenic, radionuclides), which are frequently man-made activated like heavy metals and nitrates; they are also synthetic compounds (volatile organic chemicals, nonaqueous-phase liquids), agricultural and microbiological contaminants.

Arsenic in drinking water poses a global threat affecting more than 70 countries and dozens of millions of people [55]. The number of people exposed to high level of arsenic in drinking water is likely more than estimated officially because of insufficient detection, especially in developing countries. Bangladesh, some area of India (West Bengal) is one of the worst affected regions of the world, where hundreds of thousands of people are likely to die from arsenic causing cancer of the lung, bladder, and skin. Increased content of arsenic is typical also for some regions of China, Indonesia, Philippines, North and South America (Fig. 6.3).

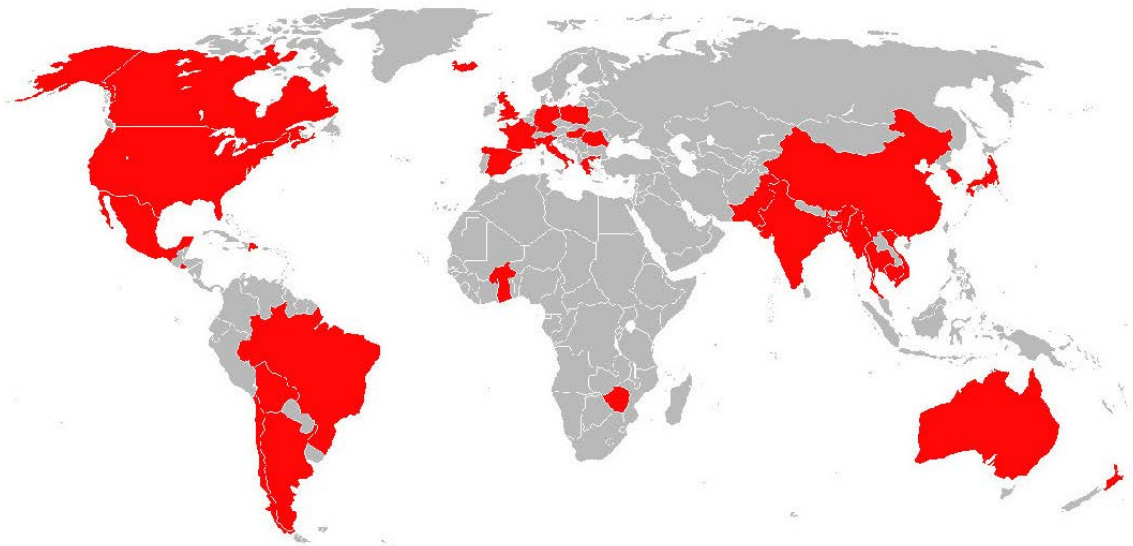


Fig. 6.3. Global arsenic distribution in ground water. The countries with natural waters containing arsenic are highlighted [76].

Arsenic poses a long-term risk and only over last decades the reliable detection has become possible in many countries. The World Health Organization (WHO) lowered the drinking water standard for arsenic to 0,01 $\mu\text{g/L}$. Many countries have not still updated their standards and retain the older guideline of 0,05 $\mu\text{g/L}$. Arsenic release is linked in some cases with the reactions between iron oxide and organic carbon. Some sulfide minerals (pyrite and arsenopyrite) contribute arsenic to ground and surface water, under certain conditions they may act either as a sink or a source of arsenic depending on local geochemistry.

Radionuclides are naturally occurring elements decaying independently on the environmental conditions and releasing radioactive energy. The decay of a radionuclide is quantified by the constant λ defined as

$$\lambda = \frac{\ln 2}{T_{0,5}}, \quad (6.3)$$

where $T_{0.5}$ is the half-life of the element or the time period required for half of the initial quantity of a substance to disintegrate.

Radioactivity of a material is measured in Becquerel (Bq) defined as one disintegration per second or in Curie (Ci, named after Pierre and Marie Curie) defined as approximate specific activity of 1 g of radium being in equilibrium with its decay products ($1 \text{ Ci} = 3,7 \cdot 10^{10} \text{ Bq}$). For some elements (uranium) radioactivity also is reported in terms of mass concentration (mg/L or $\mu\text{g/L}$).

Exposure to radionuclides increases the risk of cancer. Certain elements accumulate in specific organs, for example, Ra and Cs in the bones, iodine in the thyroid. However, naturally occurring in ground water radionuclides (f. e. Rn) can be used for health care prophylactic treatment, some artificial nuclides are also used for treatment of patients ill with cancer.

Many water sources have low contents of naturally occurring radionuclides, exceeding the level of concern to health. In some regions of the world (Russia, India, the USA) there are aquifers with elevated concentrations of natural radionuclides (U, Th, Ra, Rn) in ground water. The most dangerous are artificial radionuclides generated while processing radioactive materials required to the nuclear and other industries and handling radioactive wastes. The artificial radionuclides are used not only for power generation but also in many commercial and health care applications (detectors, medical therapy and diagnostics, measuring devices etc.).

Radionuclides contaminate ground water through leaks from radioactive ore tailings, releases of radioactive gases and liquids from nuclear power plants, testing of nuclear weapons, leaching of stored solid nuclear wastes and spills from tanks and containers placed both underground and on the ground surface. Many dangerous isotopes (^{90}Sr , ^{137}Cs) are relatively stable and, when entered to aquifers form large and long-term plums of ground water contaminations. One of the features of radionuclides is that most of them are highly toxic even at very low concentrations less than fractions of $\mu\text{g/L}$ (polonium, plutonium etc.).

Heavy metals. The metals of density greater than specific weight above 3.5 g/cm^3 to above 7 g/cm^3 including Pb, Cu, Zn, Ni, Cd, Co, Sb, Sn, Bi, and Hg refer to heavy metals according to [11]. The features of these elements are high toxicity for living organisms at low concentrations and cumulative effect or ability to accumulate in bio-chains. Heavy metals do not decay as radionuclides, they are intensively absorbed by plants, animals, and humans; eventually they are accumulated in many organs and in long time (several months or years) released from the body.

Heavy metals enter soils and ground water as a result of spills and leakages from non-ferrous and radioactive ore tailings, coal ash heaps, power plant wastes. Commonly coal, oil, diesel fuel, gasoline contain elevated amounts of heavy metals (V, Ni, Be, Pb, Hg etc.), released during combustion at high temperature. Mobility of heavy metals in ground water dramatically increases if they form complexes with organic compounds. Complexation and lower pH reduce usually high sorptivity of metals and facilitate their underground transport. Acid rains reduce pH index in topsoil; as a result, heavy metals transform from low-soluble compounds (sulfides, carbonates) to those that are high-soluble ones (hydrogen carbonate, nitrates,

hydrosulfates etc.). The sanitary limits for heavy metals in water are usually very low, some hundredths or thousandths of mg/L.

Synthetic organic contaminants are man-made (artificial) compounds used in various industries and agricultural activities, including potable water preparation [74]. Many disinfectants are used to reduce pathogenic microorganisms in water delivered by centralized systems. Unfortunately, toxic by-products of this process (for example, chloroform, bromoform) formed during the reactions of chemicals (mostly organic compounds, some of them contain chloral) with species in water cannot be removed completely. Large-scale application of these compounds may cause health risks as a result of long consumption.

Volatile organic compounds (VOCs) are the large group of synthetic contaminants. These compounds include degreasers and solvents (toluene, benzene), polychlorinated biphenyls, substances used for dry-cleaning, and gasoline compounds. VOCs are widely used in most developed countries (North America, Europe, and Japan), over last decades they have been spreading more; they have been detected at low concentrations in a number of aquifers exploited for drinking water supplies worldwide. Commonly, VOCs are hydrophobic and immiscible with water.

Non-aqueous phase liquids (NAPLs) are hydrocarbons existing as a separate phase immiscible with water. NAPLs include *light non-aqueous phase liquids* (LNAPLs) with densities less than 1 g/cm^3 , and *dense non-aqueous phase liquids* (DNAPLs) with densities greater than 1 g/cm^3 .

LNAPLs are typically the mixtures of dozens or even hundreds of petroleum and gasoline products characterized by different solubility rates. They are released from underground storages, which affect ground water quality in urban areas and near highways. LNAPLs entered the soil can migrate downward in original phase, they also may be adsorbed and react with species in ground water. The reaction products have different properties, including solubility, and then may migrate in a different way. LNAPL phase can be immobile (trapped in by an unsaturated soil) because of insufficient gravity gradient to move downward. Seasonal and other variations of ground water level can change LNAPL distribution in soils.

DNAPLs include halogenated solvents, coal tar, Polychlorinated biphenyls (PCBs), and some pesticides. They are low-soluble compounds, but their solubility exceeds sanitary limits for drinking water. DNAPLs are very common in ground water of the shallow aquifer at waste disposal sites. DNAPLs are characterized by higher mobility than LNAPLs due to greater density, which allows them to percolate into deeper aquifers (Fig. 6.4). Because of immiscibility with water and clear difference in viscosity a DNAPL phase migrates in the soil forming a finger-like front and uneven plums. Due to gravity a non-aqueous phase may accumulate on the bottom of an aquifer. Thus, DNAPL migration in heterogeneous soils forms uneven patterns of plums that are highly complicated to be described quantitatively.

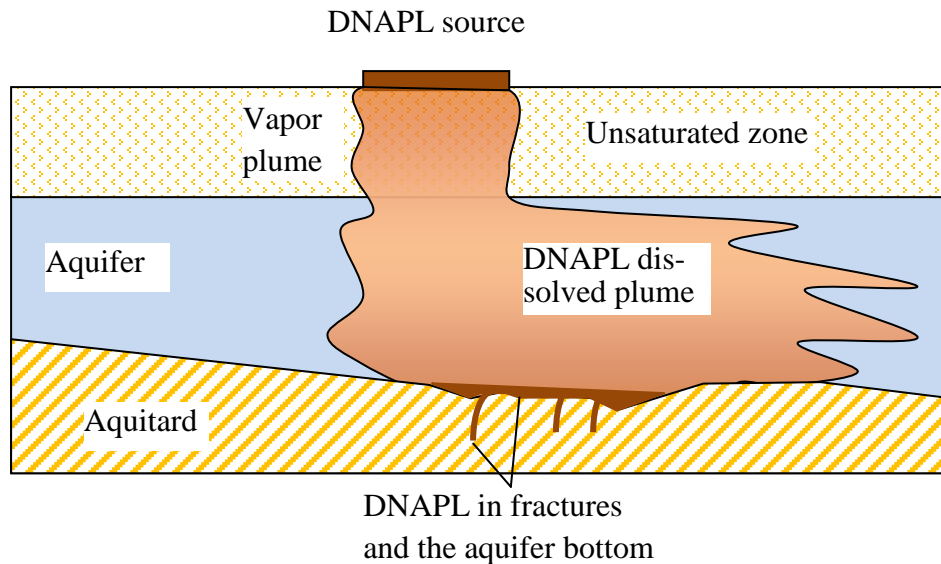


Fig. 6.4. Sketch of LNAPL and DNAPL migration in the unsaturated zone (modified from [36])

Nitrate is known to be the worldwide spread ground water contaminant, produced as a result of agricultural activities (usage of fertilizers), disposal of sewage by centralized and individual systems, leaking sewers, animal feeding operations, and acid rains [37]. Nitrate is the moist oxidized form of inorganic nitrogen. Nitrogen occurs in ground water as uncharged ammonia (NH_4), nitrite and nitrate anions (NO_2^- and NO_3^- respectively), cationic form of ammonia NH_4^+ . Cyanides can be found near waste disposal and non-ferrous ore deposits (gold, copper) mined with special acid solutions.

Nitrate is not very toxic to humans. However, under strongly reduced conditions in an alkaline environment (like in human gut) it transforms to nitrite. Nitrite ions in blood bond the hemoglobin molecules making them unable to carry on oxygen.

Domestic sewage in rural areas is commonly disposed in on-site septic systems that discharge effluents to the shallow aquifer. To avoid contamination the sewage effluents have to be removed to the basin and discharged after proper centralized wastewater treatment. Such a removal is not possible everywhere and even properly designed and constructed on-site septic systems frequently cause nitrate concentrations exceeding sanitary limits in underlying ground water.

Total nitrogen concentrations in effluents stored in septic tanks range from 25 mg/L to 100 mg/L, on the average about 40 mg/L of which about 3/4 is ammonium and 1/4 is organic [73]. As a result, septic systems contribute vast amounts of nitrogen to shallow aquifers worldwide.

Animal feedlots may lose much nitrogen as a result of ammonia volatilization, however significant amounts of nitrates percolate to ground water. The rate of nitrate discharge to ground water depends on the amount of nitrate formed from animal

wastes, the infiltration rate, and the frequency of manure removal, the animal quantity, soil properties, and temperature.

High nitrate concentrations in ground water used for drinking (of 250 mg/L to maximally 3000 mg/L) led to illnesses and deaths of both cattle and people in many countries [37]. Increased concentrations of nitrates in soils were sometimes produced by destroying natural nitrogen-fixing plants as a result of plowing the soil for farming.

Fertilizers. Organic fertilizers have been used for a long time, but they were insufficient to sustain high yields to provide growing population in the XXth century. The boom of inorganic fertilizers began after the World War II and reaches the peak during the “Green Revolution” in 1960s and 1970s. The increase in food production was accompanied by increasing application of inorganic fertilizers. The significant amounts of nitrogen (up to one half of its initial content in fertilizers) is lost to the atmosphere by denitrification and leached to surface and ground water. The excess of nitrates in the unsaturated zone continues to be the source of large-scale ground water contamination.

Since 1980s the application of fertilizers has not increased essentially worldwide; however, in European countries, North America and Australia the inorganic fertilizer application has been even decreasing. Nevertheless, Europe and the USA remain the large users of fertilizers (100 to 150 kg/ha with 50 to 55% contents of mineral components). In contrast, most developing countries use less than 10 kg/ha [68].

Organic fertilizers of animal origin contain many essential nutrients including nitrogen, phosphorus, and potassium; when improperly used they may cause ground water contamination similar to that resulted by inorganic fertilizers.

Pesticides. The term “pesticide” refers to any chemical that kills pests and includes insecticides, fungicides, and herbicides. Natural pesticides in form of plant extracts were used thousands of years ago to protect crops from insects and fungus. Since the mid of the XXth century wide application of pesticides began both in rural and urban areas. Currently the use of pesticides in developed countries ranges from 1 to 3 L/year of insecticides and from 3 to 10 kg/year of fungicides. In developing countries pesticide application is limited primarily for financial reasons; however, last decades show the trend of growing application of chemicals in agricultural production in Asia and Africa.

Pesticides used in the mid of the XXth century (DDT, dieldrin and other chlorinated hydrocarbons) were low-soluble in water, strongly sorbed by soils and had broad spectrum of harmful effects. These compounds accumulated in soils and adversely affected aquatic ecosystems because of persistence and accumulation in bio-chains. Nevertheless, due to high sorptivity only small amounts of old pesticides reached aquifers.

New pesticides are much more soluble, less sorbed, more biodegradable, and have selective toxicological effects. Consequently, in spite of declining pesticide application in developed countries, up-to-date pesticides having higher solubility and mobility may result in large-scale ground water contamination. Many compounds are implied to be degraded on the ground surface under oxidizing conditions. When

accumulated at the bottom of surface water bodies and in wetlands under reducing conditions new pesticides remain stable for long time in initial forms toxic to humans and animals.

Despite the regulatory restrictions and prohibiting the use of some pesticides their residuals and decay products are still in ground water in the areas of former extensive applications. Moreover, many unused or forbidden chemicals are exported to developing countries or still produced there because of the absence of stringent environmental limitations. This process leads to expanding ground water contamination, primarily, in shallow aquifers worldwide.

A number of pesticides contain arsenic as an active component to prevent from insects and fungus. Besides, arsenic is a species of some inorganic chemicals applied in agriculture, for example, phosphate fertilizers. The wide and long-term application of these chemicals on large areas in agriculture also contributes to soil and natural water contamination.

Due to large-scale ground water contamination individual water supply systems in rural areas of intensive agriculture may be even more unsafe than centralized municipal systems in urban areas.

Concentrated animal feeding operations produce elevated concentrations of nutrients, metals, bacteria, and a number of pathogens. Many of infectious organisms causing illnesses of animals can also cause disease in humans and can survive in water. The pathogens posing risks to humans (*Salmonella spp.*, *Escherichia coli*, *Campylobacter spp.*, *Listeria monocytogenesis*) and some viruses and protozoa (*Chryptosporidium parvum* and *Giardia*) have been found in aquifers near urban areas used for drinking purposes [54]. Recently antibiotic-resistant microorganisms have been discovered in ground water near swine facilities [57]. This may result in spreading of antibiotic resistant pathogens to water supply systems. According to [5] pathogens in ground water may persist and stay alive at least 400 days.

Microorganisms and organic compounds in ground water. Microorganisms in the subsurface consist of bacteria, protozoa, and fungi. *Bacteria* are single-celled organisms metabolizing dissolved organic matter of natural or artificial origin. *Protozoa* are larger unicellular organisms with animal-like behavior when moving. Fungi are multi-cellular organisms; the walls of fungal cells contain chitin unlike the cell walls of plants, protozoa, and bacteria. Fungi can degrade organic matter and are used for recycling wastes.

Bacteria can enter ground water in different ways. Some of them can move with flagella in response to the gradient of concentration in solution, which could be an indicator of detecting the zones of spreading contaminants. Typically bacteria are immobile, and fixed to the surface of solids in porous material. Bacteria on the surface form a *biofilm* that is a film often attached to the surface. Transformation reactions reducing concentrations of contaminants occur mainly in biofilms due to low fluid velocity (Fig. 6.5)

There are various methods to quantify microorganisms in aqueous solutions. A plate count implies smearing a water sample on a special media, incubating and counting the bacteria. The result of testing is measured in colonyforming units per

milliliter (CFU/mL) for liquid samples or CFU/g of a dry sediment. This kind of measurement requires direct counting using a microscope.

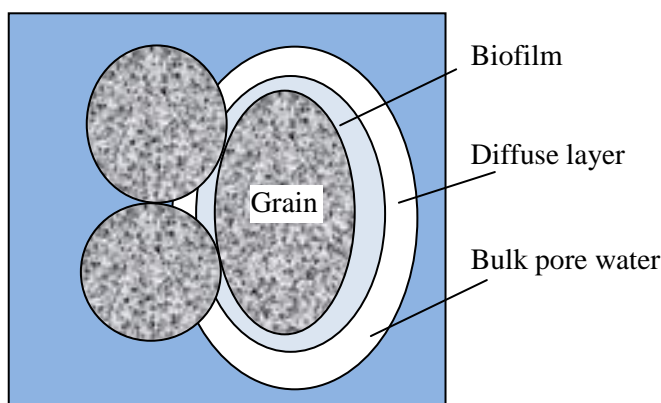


Fig. 6.5. Biofilms [8]

In undisturbed aquifers bacteria population density ranges from 10^5 to 10^7 per gram of dry weight [21]. The population densities of bacteria in topsoil and the shallow aquifer are much greater and commonly become lower in depth due to the decrease in organic matter content. However, there are many deviations from this trend, for example, in underground openings, mine waters, and heterogeneous soils.

It was established that the zones of higher conductivity of soils and rocks are more populated by bacteria than low-permeable zones [38]. Bacteria are more abundant in sandy sediments; in contrast, bacteria populations in clay sediments are considerably less abundant. This fact can be explained by difficulties in colonizing fine-grained materials of lower permeability compared to coarse permeable material more accessible to microorganisms migrating in ground water.

Bacteria play the key role in degrading organic contaminants in ground water. In the presence of oxygen aerobic reactions occur, anaerobic reactions take place in the absence of oxygen, this influences degradation condition of different compounds (Table 6.4). Microorganisms use the organic matter as the feed source and produce energy in the process of transferring electrons in redox reactions.

Table 6.4

Decomposition conditions for bacteria [59]

Conditions	Substrates
Aerobic and anaerobic	Glucose, acetone, acetate, phenol
Aerobic primarily	Benzene, toluene, xylene, methane, propane

Silver nanoparticles are used in many products because of their ability to kill bacteria, damage microbial membranes without harming human cells [49]. These particles enter the environment commonly as a by-product of sewage treatment plants. Nanoparticles cannot be filtered and remain in wastewater treatment "sludge", which is spread on agricultural lands as a fertilizer. Thus, spreading of silver

nanoparticles can significantly inhibit biodegradation and reduce the cleaning ability of soils.

Nanosilver is highly toxic to aquatic life. Although silver is safer for people than other trace elements such as lead and chromium, it may hurt aquatic organisms. Silver is toxic to many fresh- and salt-water organisms (from phytoplankton to different types of fish, especially in their initial stages). One of the main sources of silver is the special clothes treated with nanoparticles; those clothes lose silver through breakdown and leach when cleaning in washing machines. Many waterways were charged by silver introduced by the photography industry during last decades. New silver nanoparticle products may result in highly toxic levels of silver being reintroduced into rivers and lakes through water treatment facilities. Silver particles may damage active bacteria and lead to inability of active sludge of treatment plants cleaning wastewaters. Further application of nanosilver may cause bigger environmental problems and, perhaps, has to be limited.

Drinking water standards include primary and, in some countries, secondary drinking water standards. Primary standards establish the ranges for the contents of major constituents in ground water (see Routine analysis in Section 6.1) and limit the levels of specific contaminants that can adversely affect public health and may occur in water.

These standards use the term *maximum contaminant level* (MCL) or sanitary limit defined as that does not cause any known adverse health effects. The MCLs are sometimes set at a level that cannot be met due to local hydrogeological features, for example, naturally increased content of arsenic or radionuclides. Many hazardous compounds, like carcinogens and microbiological contaminants have zero MCL because their safe level is frequently impossible to determine.

In case if there is no reliable method economically and technically feasible to measure contaminants at low concentrations (for example, microbiological contaminants) the so-called treatment techniques (TT) are established. These techniques are a feasible procedure of the level of technological performance that public water systems must follow to ensure the control over the contents of hazardous compounds. For instance, withdrawn ground water or surface water has to be pre-treated to limit the content of pathogens.

Drinking water standards have to be regularly updated because

- a) the number of contaminants released to the aqueous environment continues to grow;
- b) applied medicine is accumulating experience and knowledge related to adverse impacts of contaminants on public health, and
- c) the progressing analytical equipment enables us to detect lower concentrations of wider range of compounds.

The maximal concentrations according to the drinking water standards in Ukraine are brought together in Table 6.5. Besides, the pH index is limited by the range 6,5–8,5, water hardness has to be less than 7 mmol/L, TDS has to be less than 1000 mg/L.

Table 6.5

Maximal allowed content of major, minor and trace constituents in water [48, 52]

Component	Maximal concentration, mg/L	Component	Maximal concentration, mg/L
Major constituents			
SO_4^{2-}	250	Ca	100
Cl^-	250	Mg	30
NO_3^-	45	Na	200
		K	20
Minor and trace constituents			
Fe	0,2	Cu	1
Mn	0,05	Zn	1
Al	0,2	Ba	0,1
NO_2^-	0,1	Be	0,0002
Ammonium	0,5	B	0,5
Cd	0,001	Ni	0,02
As	0,01	Hg	0,0005
Perchlorate ClO_4^-	0,01	Pb	0,01
Se	0,01	Sr	7
Sb	0,005	F	0,7–1,5 depending on climate
Tl	0,0001	Cyanides CN^-	0,05
Cr	0,05		
Organic compounds			
Benzo(a)pyren	0,00001	Benzyl	0,001
Pesticides (total)	0,0005	Surfactants	0,1
Oil products	0,05	Chlorophenol	0,0003

6.3. Basic chemical reactions in ground water

Acid-base reactions. Complexation. Surface reactions. Ion exchange. Oxidation-reduction (redox) reactions.

A number of chemical reactions occurring in ground water have significant impact on water composition and control the mobility of contaminants. These reactions include acid-base reactions, oxidation-reduction, precipitation and dissolution, sorption and desorption, complexation and some others.

Acid-base reactions involve the transfer of hydrogen ion H^+ among the ions in the aqueous phase (Table 6.6). The concentration of the hydrogen ion determines pH of solution, which controls many processes in saturated soils and rocks. Many

compounds, including heavy metals and other contaminants become very mobile at low pH because rocks and soils adsorb usually much less amounts of those compounds from acidic solutions compared to neutral or alkaline environment. At high pH values the metals tend to precipitation and adsorption, which decreases their concentrations in ground water.

Table 6.6

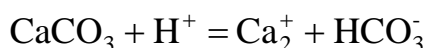
Important acid-based reactions in natural water systems

Reaction	Mass law equation	$-\log K$ (25 °C)
$H_2O = H^+ + OH^-$	$K_w = (H^+)(OH^-)$	14,0
$CO_2(g) + H_2O = H_2CO_3(aq)$	$K_w = \frac{(H_2CO_3)}{P_{CO_2}(H_2O)}$	1,46
$H_2CO_3(aq) = HCO_3^- + H^+$	$K_w = \frac{(H_2CO_3^-)(H^+)}{(H_2CO_3)}$	6,35
$HCO_3^- = CO_3^{2-} + H^+$	$K_w = \frac{(CO_3^{2-})(H^+)}{(HCO_3^-)}$	10,33

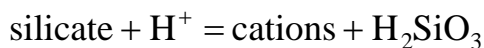
g = gaseous phase, aq = aqueous phase.

The equilibrium constants of acid-base reactions are the indexes quantifying the distribution of different species in aqueous solution depending on pH. Below is the example that illustrates this calculation.

Another group of acid-base reactions involve the reaction of minerals with hydrogen ion, for example, dissolution/precipitation of calcite



or dissolution/precipitation of calcite of silicate minerals



Many amazing landforms and caves around the world are the result of dissolution of calcite ($CaCO_3$) with ground water and adds Ca^{2+} and HCO_3^- to the ground water.

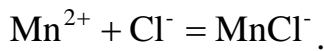
Dissolution and precipitation reactions are the reactions when natural salts like halite, gypsum, and anhydrite dissolve or precipitate. This influences both mineral and ion distributions in solutions. For halite this reaction is written as follows:



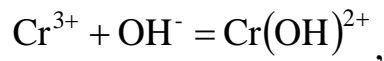
Complexation. A complex is an ion formed by combining simpler cations, anions, and sometimes molecules. The cation or central atom is typically one of a large number of metals from the periodic table. The anions, often called *ligands*, include many of the common inorganic species in ground water (Cl^- , F^- , Br^- , CO_3^{2-} , PO_4^{3-} , SO_4^{2-}). The ligand may also comprise various organic molecules such as amino acids. Complexation facilitates the transportation of metals in ground water. Naturally occurring metals like Pb and Zn, transported for a long time in some aquifers can create ore deposits. Complexation plays the key role in transporting toxic metals such as Cd, Cr, Cu, U, Pu and others far away from the plume. Metals occurring as free metal ion are typically not mobile because of intensive adsorption in clay minerals.

The examples of complexation reactions are given below.

1. Simple combination of a metal ion and a ligand



2. Complexes formed when complexes combine with ligands



Here a ligand is an ion or molecule (functional group) that binds to a central metal atom to form a chemical complex.

Surface reactions can changes the geochemistry of natural and contaminated ground water. They involve reactions between ions in solution and the grains of crystals in rocks or sediments. For example, water in clayey marine deposits may lose Ca and Mg and gain Na due to cation exchange, which commonly softens water similar to the same process in commercial softeners. The property of some contaminants to be adsorbed on soil or rocks retards their transportation in ground water.

When water is mixed with the porous solids, a dissolved constituent at a low concentration C is distributed between the solution and the solid after a time needed to reach the equilibrium. This process is described by the equation [59]

$$S = \frac{(C_i - C_{eq})V_s}{M_s}, \quad (6.4)$$

where C_i is the initial concentration, g/cm^3 ; C_{eq} is the equilibrium concentration, g/cm^3 ; V_s is the solution volume, cm^3 ; M_s is the sediment mass, g; S is the mass adsorbed on the surface, g/g. Each experiment produces a single point on the plot “ S versus C ” (Fig. 6.6). Repeating this experiment at the same temperature with different values of C enables plotting the family of points forming the sorption isotherm. The experimental isotherms (Table 6.7) have no prescribed shape.

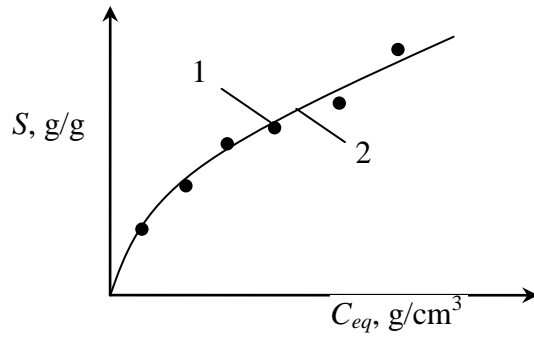


Fig. 6.6. An experiment sorption isotherm: 1 – experimental data, 2 – the isotherm, for other notations see Eq. 6.4.

Table 6.7

The most applicable isotherms

Isotherm	Proposed/derived by
$S = kC^n$	Freundlich
$S = \frac{Q_0 k C}{1 + k C}$	Langmuir
$S = K_d C$	Henry

In Table 6.7 k is the partition coefficient, n is the empirical constant ranging from 0,7 to 1,2, Q_0 is the maximum sorptive capacity for the surface, K_d is the distribution coefficient. Larger values of k and K_d are indicators of greater sorptivity of soils.

Example. Calculate the mass of an adsorbed substance in two soil samples using the results of two measurements presented in Table below.

#	$C_i, \text{g/cm}^3$	$C_{eq}, \text{g/cm}^3$	V_s, cm^3	M_s, g
1	$5 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	10	15
2	$1 \cdot 10^{-3}$	$8 \cdot 10^{-4}$	10	15

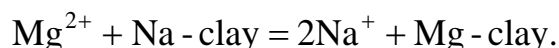
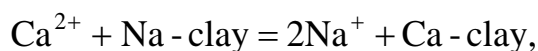
Substituting the results of the experiment into Eq. 6.4 yields

$$S_1 = \frac{(5 \cdot 10^{-4} - 4 \cdot 10^{-4}) \cdot 10}{15} = 6,7 \cdot 10^{-5} \text{ g}$$

$$S_2 = \frac{(1 \cdot 10^{-3} - 8 \cdot 10^{-4}) \cdot 10}{15} = 1,34 \cdot 10^{-5} \text{ g}$$

Assuming that Henry isotherm is valid, the distribution coefficient is equal $K_d = 10 \text{ cm}^3 / 15 \text{ g} = 0,67 \text{ cm}^3 / \text{g}$.

Ion exchange. Mineral surfaces often bind ions, however, bound ions can exchange with ions in solution, for example,



This kind of exchange may dramatically change the chemistry of water. As a result of water-softening reactions Ca and Mg ions exchange with Na ions adsorbed onto clay minerals. High concentration of Ca+Mg makes water hard; this water tastes better than soft water but is not good for washing. In terms of contamination problem ion exchange can inhibit transportation of contaminants, particularly, heavy metals and radionuclides, in ground water reducing their mobility due to binding onto minerals.

Clay minerals carry a significant negative surface charge. Cations bound to the clays can exchange with cations in ground water (Fig. 6.7). The negative charge in the clays is due to substitutions of cations of lower valence (for example, Al^{3+} for Si^{4+} in the lattice) and, partially, because of the broken bonds at the edge of minerals.

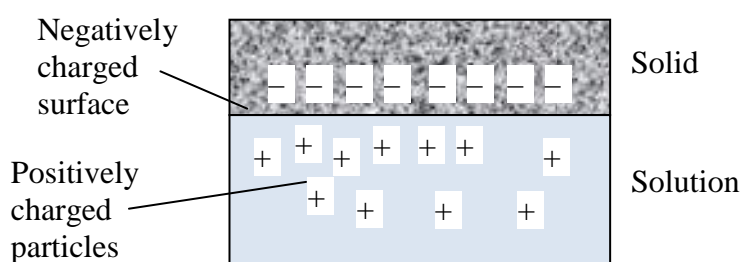


Fig. 6.7. Scheme of ion exchange near solid surface of clay minerals [59]

Oxidation-reduction (redox) reactions are very important in controlling the geochemistry of natural waters. They differ from other reactions because they involve the transfer of electrons and are mediated by microorganisms that play the role of catalyst speeding up the commonly slow reactions.

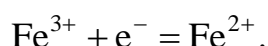
Redox reactions involve elements such as carbon, oxygen, iron, nitrogen, and others that are able to gain or lose electrons. These elements have different oxidation states, for example +IV for carbon, -II for oxygen.

Oxidation is the removal of electrons from an atom, forcing a change in the oxidation number of an element, for example,



where e^{-} is an electron. The oxidation number of Fe^{2+} changes from (+II) to (+III).

Reduction is the addition of electrons to lower the oxidation number, for example,



All redox reactions transfer electrons from a reductant (electron donor) to an oxidant (electron acceptor). Thus, redox reactions produce no free electrons.

Section review

1. Explain the difference between cations and anions.
2. Explain the difference between molar and molal concentrations.
3. Compare mass per mass and mass per volume concentrations. Which concentration scale is more applicable?
4. How are the major and minor constituents in ground water defined?
5. What are the trace elements? What kind of chemical elements are they mostly?
6. Define the ranges of fresh, brackish, salt and saline water.
7. Identify the sources of organic matter in ground water.
8. What dissolved gases are the most abundant in ground water?
9. Describe the typical patterns of vertical zoning of oxidation/reduction and salinity.
10. What ions are called major ions? Why?
11. Explain the physical sense of the pH index.
12. Explain the physical sense of the Eh index.
13. Give the examples of redox reactions.
14. Which elements are measured in routine analysis of water?
15. What are the major sources of water contamination?
16. How can water contamination be discovered and assessed?
17. Characterize point and non-point sources of ground water contamination.
18. Describe the ways and content of contaminants migrating from fuel storages.
19. Describe the ways and content of contaminants migrating from waste disposal and landfills.
20. Describe the ways and content of contaminants migrating from domestic septic system and impoundments.
21. Characterize injection wells as the conduits for contamination in aquifers.
22. Characterize ground water contamination caused by agricultural activities linked with animal production.
23. Characterize ground water contamination caused by agricultural activities linked with crop growing.

GLOSSARY¹

Acidic Having a pH below 7,0.

Adsorption Attraction and adhesion of ions or molecules in solution to the surface of solids.

Advection Mass transport process controlled solely by the bulk motion of the flowing ground water.

Air entry pressure Small negative pressure head existing when the moisture content in a porous geological material is equal to the porosity.

Alkalinity Capacity of bases to neutralize acids.

Alluvial aquifer Aquifer in sediments deposited by a river.

Anisotropy State of which physical properties, such as hydraulic conductivity, vary with direction.

Anthropogenic Influenced or created by humans.

Aquiclude Low permeability geological unit that, although porous and able to absorb water and contaminants, is incapable of transmitting significant quantities of water.

Aquifer Saturated, permeable geologic unit that is capable of yielding economically significant quantities of water to wells and/or springs.

Aquitard Low permeability geological material that retards, but does not completely halt, ground water flow through it. It does not yield water in significant quantities to wells and/or springs, but can be a significant source of ground water storage.

Aridity Climate characterized by low annual levels of precipitation.

Artesian water Ground water held in porous media under significant hydrostatic pressure such that its hydraulic head is greater than the elevation of the bottom of the confining layer of the aquifer.

Artificial recharge Anthropogenic process of adding recharge to an aquifer.

Background level Naturally occurring concentrations of substances in air, water, or soil.

Bedrock General term applied in bulk to the consolidated geological material in the earth. It may contain and transmit ground water through primary and secondary porosity.

Borehole Circular hole made by boring with an auger or other intrusive method. Commonly denoting a hole driven to obtain a geologic sample or to place a well.

Brackish water Water with a salinity intermediate between sea water and fresh water (between 1,000 and 10,000 mg/L of dissolved solids)

Brine Water with a high content of dissolved solids.

Capillarity Rise or movement of water in the interstices of soil or rock as a result of surface tension.

Capillary height Height to which water will rise in a capillary tube due to capillary forces.

¹ The definitions of terms follow [51]

Capillary pressure Pressure of fluids under the influence of surface tension and adhesion.

Capillary water Water held in place by capillarity, or propelled by capillary motion.

Catchment area Surface area contributing recharge to an aquifer.

Cementation Filling of voids in a sediment with precipitated minerals, such as silica, calcite, and iron oxide.

Chemical weathering Chemical processes (hydrolysis, hydration, carbonation, ion exchange, and solution) that break down rocks and minerals into more stable minerals in the given environment.

Clay soil Soil containing more than 40% of clay, less than 45% of sand, and less than of 40% silt.

Coefficient of compressibility Relative decrease in water volume per unit increase of pressure at a given temperature.

Colloid Fine-grade in suspension, or that can be easily suspended.

Complex Dissolved species that is formed by the reaction of two or more similar soluble species.

Conductivity Ability of a geological material to transmit a fluid.

Cone of depression Depression of hydraulic heads around a pumping well caused by withdrawal of water.

Confined aquifer Aquifer bounded above and below by an aquitard. Water in a confined aquifer is under pressure greater than atmospheric pressure.

Confining layer (unit) Material of low hydraulic conductivity that is stratigraphically adjacent to one or more aquifers.

Constituent Chemical or biological substance in water, sediment, air, or biota that can be measured.

Darcy Standard unit of permeability named after the French engineer who lived in the XIXth century that discovered the law of porous media flow.

Density dependent flow Ground water flow induced by density gradients.

Desorption Process of removal of an absorbed or adsorbed substance.

Diffusion Movement of suspended or dissolved particles, due to kinetic of thermal energy, from a more concentrated to a less concentrated area.

Discharge 1. Volume of water flowing in a stream or through an aquifer past a specific point in a given period of time. 2. The volume of water being pumped from a well, or flowing from a pipe or any other type of outfall.

Discharge area Area in which there is an upward component of hydraulic head in the aquifer. This may result in discharge of ground water to surface.

Dissolved solids Minerals and organic matter dissolved in water.

Divide An imaginary line separating ground water flow in different directions.

Drainage 1. The movement of water from one area to another in response to gravity. 2. Runoff of water from a given area that flows into surface streams or subsurface conduits.

Drinking water standard Standard for the threshold concentration of a constituent or compound in a public drinking water supply, which is not a legal regulatory guideline, but is used as an advisory guideline.

Dual porosity Term used to describe porosity in an aquifer with a bimodal void distribution in (1) fracture pore volume and (2) grain or rock pore space.

Effective porosity Volume of interconnected pore space through which water can flow in a geologic medium divided by the total volume of the medium.

Effluent 1. General discharge of liquid or gaseous waste to the environment.
2. Liquid waste discharged from a manufacturing or treatment process.

Equipotential line Contour line on the water table along which the pressure head of ground water is the same. Fluid flow is normal to these lines in the direction of decreasing fluid potential.

Fault Fracture in geologic material along which displacement has occurred parallel to the plane of the fracture. A fault may act as a barrier to the movement of ground water, but can also act as a conduit.

Fixed ground water Ground water held in saturated material with interstices small enough to hold water to pore walls, thus making it unavailable as a source of water pumping.

Flow line Line indicating the idealized path taken by ground water towards a discharge location under steady-state conditions. Flow lines are perpendicular to equipotential lines in isotropic media.

Fossil water Interstitial water that was buried at the same time as the original sediment.

Fracture Fault, joint, or any other crack in rock due to structural stresses.

Free water Water in soil or rock that is free to move in response to pull of gravity.

Fully penetrating well Well drilled to the bottom of an aquifer and withdrawing water from the entire saturated thickness of the aquifer.

Geologically bound water Water which presumably has been in storage since the beginning of the Earth or for a geologically significant amount of time and is not a part of hydrologic cycle.

Grain size General dimensions, such as average diameter or volume, of particles or mineral grains in a geologic material that comprises a geologic medium, assuming that the particles are spheres for the purpose of measurements.

Ground water 1. Water occupying voids in a geologic medium. 2. The water in the zone of saturation, below the water table in a confined or unconfined aquifer held at pressure equal to or greater than atmospheric pressure.

Ground water basin Aquifer or system of interconnected aquifers having well-defined boundaries and more or less definite area of recharge and discharge.

Ground water runoff Portion of runoff that infiltrates the subsurface to become ground water and discharges into a stream channel as spring or seepage water.

Ground water yield Maximum sustainable pumping rate without a substantial drop in hydraulic head in an aquifer.

Heterogeneous Having different characteristics in different locations. In hydrogeology this term refers to porosity and hydraulic conductivity.

Homogeneous (uniform) Having the same characteristics in different locations.

Hydraulic conductivity Coefficient of proportionality describing the rate of fluid flow for an isotropic porous medium and homogeneous fluid.

Hydraulic gradient Change of total head divided by the change in distance in the direction of the greatest change.

Hydraulic head 1. Potential energy per unit weight of a fluid. 2. Sum of elevation head and pressure head.

Hydraulic properties Properties of soil and rock that govern the capacity to hold and transmit water (effective porosity, specific retention, hydraulic conductivity, and storativity)

Hydrogeological cycle Process of recycling water from the atmosphere to the earth and vice versa.

Hydrosphere All water contained by the Earth as separate from the lithosphere, biosphere, and atmosphere. The hydrosphere includes all ground water and surface water bodies, and all forms of precipitation.

Immiscible liquids Liquids that do not mix with water.

Immobile water One of three types of water: crystalline water bound in minerals; adsorbed water, referred to as hygroscopic water; water in non-connected pores in the subsurface.

Ion exchange Reversible process in which an ion in solution in contact with a crystal replaces an ion in the lattice of that crystal without destroying the crystal structure or electrical neutrality.

Juvenile Descriptor of water, gas, or other fluid that is derived from a magma or from a cosmic source and is new to the Earth hydrosphere.

Karst Geological formation or landscape formed through dissolution and collapse in carbonate material that is characterized by irregular dissolution features such as sinkholes (dolines), caves, and underground drainage.

Laminar flow Flow type in which the fluid particles move in ribbon-like paths, with no intermixing between layers.

Leaching Dissolution of soluble constituents from soil or rock.

Leachate Solution obtained by water percolating through soil or other material containing soluble substances and that contains amounts of these substances in solution.

Leakage Flow of water from one hydrogeological unit to another.

Leaky aquifer Aquifer bounded by combination of aquitards or an aquitard and aquiclude.

Liquefaction Process occurring when saturated sediments are shaken by an earthquake, or any other form of natural or anthropogenic seismic wave generation, causing the sediments to lose grain-to-grain contact and strength, thus causing collapse of structures with foundations in the sediment.

Lithology Mineralogy, grain size, texture, and other physical properties of granular soil, sediment, or rock.

Loam Permeable soil composed of a mixture of clay, silt, sand that is rich in organic matter.

Loess Homogeneous, commonly non-stratified, porous, friable, slightly to strongly cohesive, fine-graded blanket of wind-blown and wind deposited silt and fine sand.

Lyzimeter Device for measuring pore moisture or evapotranspiration in the field. It contains a soil column, vegetation, and measuring devices.

Mass transport Carrying of material, other than the carrying fluid itself, in a fluid medium such as water, air, or ice.

Mineral water Water containing naturally or artificially supplied mineral salts and gases.

Moisture content Moisture in a given soil mass, expressed as weight of water divided by weight of oven-dried soil.

Multiphase flow In ground water flow, flow of two or more immiscible fluids of different densities.

Partially penetrating well Well drilled partially into an aquifer and withdrawing water from a fractional part of the total thickness of the aquifer.

Pathlines Generalized flow path that a particle will follow in a flow region during a steady or transient event.

Perched aquifer Locally saturated zone overlying a low-permeability unit in the otherwise unsaturated zone.

Percolation Infiltration of water downward (or possibly upward) and radially under hydrostatic pressure through the interstices of a geological material usually to the saturated zone.

Permeability Measure of the ease with which a fluid moves through porous medium that is dependent upon the physical properties of the medium itself, and not upon the fluid being transmitted.

Phreatic cycle Period of time (daily, annually, etc.) during which the water table rises and then falls.

Piezometer Non-pumping well, generally of small diameter, that is used to measure the elevation of the water table.

Plume Well-defined, mobile zone of contaminated ground water containing dissolved contaminants.

Pollutant Substance introduced into water, soil, or air that adversely affects the usefulness of resource or impairs the health of living organisms.

Pore Small-diameter opening in a geologic material.

Porosity Volume of porous space in a porous geologic medium divided by the total volume of that medium. Porosity is usually reported as a decimal fraction.

Precipitation Water in any form that falls to the surface of the earth from the atmosphere.

Pressure head Height of the fluid column capable of being supported by hydrostatic pressure at some point within the fluid.

Radial flow Flow of water in an aquifer towards a vertically oriented pumping well.

Recharge Process of replenishment of water to the saturated zone by downward infiltration of water from rainfall, streams, and other sources.

Redox Shortened term for oxidation-reduction (redox potential).

Reservoir Subsurface volume of porous and permeable geologic material storing water.

Retained water Interstitial water held in porous medium by molecular attraction against gravity, in isolated interstices, or as water vapor in interstices after drainage.

Saline water Water with a dissolved solid concentration greater than 10,000 mg/L.

Salinity Total quantity of dissolved salts in water, usually measured in parts per thousand.

Salt water intrusion (encroachment) Intrusion of salt water into fresh surface or ground water. The fresh water is generally displaced by salt water of greater density.

Sandstone Sedimentary rock composed of sand-sized particles set in a fine-grade matrix (silt or clay) and more or less firmly united by a cementing material.

Saturated zone Subsurface zone in which the voids in a porous geological material are filled with water.

Saturation Condition of a geological material in which interstices are filled with a fluid, usually water, and applies whether the liquid is under greater than or less than atmospheric pressure.

Sedimentation Process of forming or accumulating sediment in layers.

Seepage Process involving the slow movement of water or other fluid through a porous material.

Seepage face Area where water emerges from a slope at atmospheric pressure and flows downward, usually to a stream.

Semiarid Transition zone climate with slightly more precipitation than in arid climate, and where sparse short grasses and draught resistant shrubs are the characteristic vegetation.

Soil moisture Water contained in the interstices of the unsaturated zone.

Solute Generally, one component in a solution that is present in a smaller volume than the solution.

Specific capacity Measure of well productivity calculated by dividing the rate of discharge from a well by the corresponding drawdown of the water level in the well.

Specific storage Volume of water that a unit volume of aquifer releases from, or takes into, storage under a unit change in hydraulic head.

Specific yield Volume of water that an unconfined aquifer releases or takes into storage per unit surface area per unit change in the level of the water table.

Storage capacity Volume of pore space in a porous geological medium that can be used to store ground water.

Subsurface runoff Ground water that moves through the unsaturated zone and discharges to a stream and behaves more like overland flow than base flow.

Surface runoff Water that flows across the land surface without infiltrating the soil; this occurs when surface materials are impermeable or saturated.

Total dissolved solids (TDS) The quantity of dissolved material in a sample of water, either the residue evaporation or the sum of the chemical constituents.

Transient flow Flow conditions, the magnitude or direction of which change over time.

- Turbulent flow** Flow in which the water particles intermix and follow irregular paths through pores.
- Unconfined aquifer** Aquifer with no confining beds between the saturated zone and the surface and in which water is free to fluctuate under atmospheric pressure.
- Uniformity coefficient** Ratio of the grain size that is 60% finer by weight to the grain size that is 10% finer by weight on the grain size distribution curve. It is used as an indicator of sediment heterogeneity.
- Unsaturated zone** Zone between the ground surface and the water table, where fluids are held temporarily or permanently under pressure less than atmospheric pressure.
- Water content** Weight of water contained in a porous geologic material divided by the dry weight of the material.
- Water demand** Water requirements for a particular purpose, such as irrigation, power, municipal supply, or storage.
- Water quality** Chemical, physical, and biological characteristics of water with respect to its suitability for a particular purpose.
- Water solubility** Maximal concentration of a chemical compound that can be dissolved in a given water body or system.
- Well** Dug, bored, or drilled excavation, or driven shaft, typically cylindrical, with the purpose of observing or withdrawing water from an aquifer or for injection of fluids below ground.
- Wetland** Area transitional between terrestrial and aquatic systems that is periodically or continually inundated or saturated with surface or ground waters on an annual or seasonal basis.

NOMENCLATURE

A	Area, m^2
b	Aquifer thickness, m
C	Concentration of a solute or solid in solution, g/m^3 (mg/cm^3)
d	Unit of time in hydrogeology, d = day
E	Evaporation, m^3/d
eq/L	Unit of equivalent charge concentration
g	Gravitational constant, $9,81 m/s^2$
H	Hydraulic head of ground water flow, m
h_p	Pressure head of ground water flow, m
i	Hydraulic gradient, dimensionless
K	Hydraulic conductivity, m/s or m/d
k	Partition coefficient of adsorption equilibrium, dimensionless
K_d	Distribution coefficient between solid and liquid phase in saturated soil/rock, mL/g
M	Mass, kg
	Molar concentration, mol/L
n	Porosity, dimensionless
P	Precipitation, m^3/d
p	Pressure, Pa
Q	Discharge (inflow or outflow), m^3/d
q	Specific discharge of ground water flow, m/d
R_N	Ground water recharge, m^3/d
S	Storativity, m^3/m^3
S_s	Specific storage, 1/m
S_y	Specific yield, dimensionless
T	Temperature, $^{\circ}C$
	Transmissivity of an aquifer, m^2/d
TDS	Total dissolved solids or mass of solids dissolved in water solution, g/L
V	Volume, m^3 (or L or cm^3)
z	Vertical coordinate, m
	Elevation above datum, m
β	Compressibility of water or rock, m^2/N
Δl	Distance between two points, m
ε	Evaporation rate, mm/d (mm/a)
κ	(Intrinsic) Permeability, m^2 , darcy
λ	Decay constant of radionuclides or other decaying species, 1/s
μ	Dynamic viscosity of water, kg/(m·s)
ρ	Density, kg/m^3
θ	Water content (saturation) of soil, % or dimensionless
Ψ	Water potential of unsaturated soil, Pa or m
ψ	Suction pressure, Pa or m

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